Supporting Information

Visible-light Driven Bioorthogonal Photoclick Reaction of *o*-Diones with Vinyl Amides

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Contents

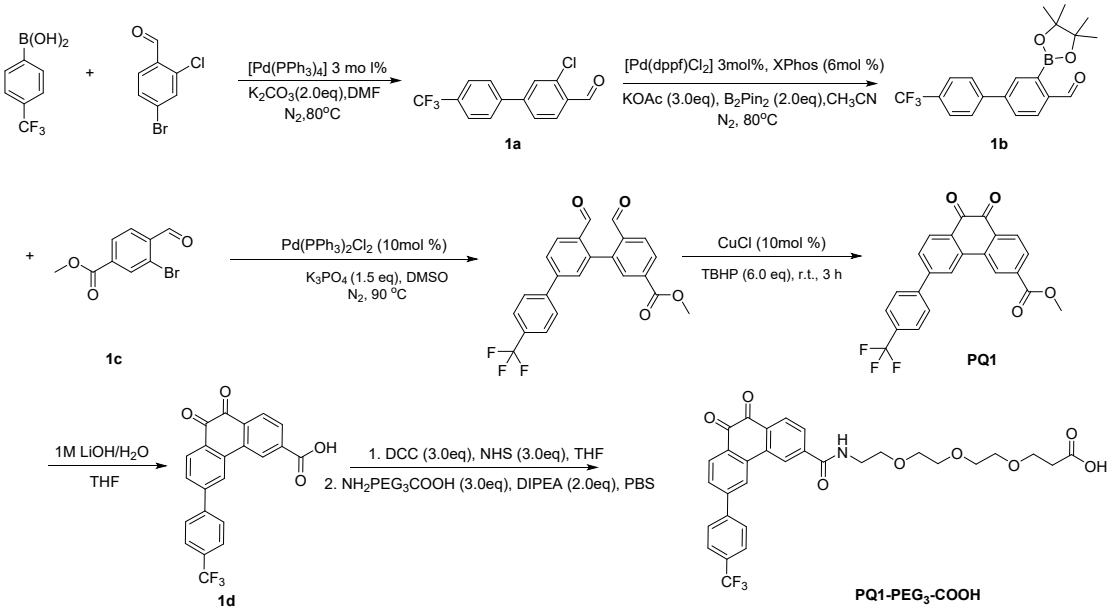
Materials and Methods

1. General materials and methods

All chemicals and solvents were purchased from J&K chemicals (Shanghai, China), Energy Chemical (Shanghai, China), TCI (Shanghai, China) or Sigma-Aldrich (Shanghai, China) unless otherwise indicated. High glucose Dulbecco's Modified Eagle's Medium (DMEM), fetal bovine serum (FBS), penicillin/streptomycin, BCA protein assay kit were purchased from Thermo (Shanghai, China). Coomassie staining kit was purchased from Beyotime (Shanghai, China). Bovine serum albumin were purchased from Energy Chemical (Shanghai, China). Light source: a Xenon Lamp CEL-PE300L-SA (Zhong jiao Jin yuan, China), a LED illumination system (Taobao, China). ^{1}H NMR and ^{13}C NMR spectra were obtained on a 400 MHz Bruker AVANCE III–400 spectrometer, 500MHz Bruker AVANCE III HD spectrometer and 600MHz Bruker AVANCE III HD spectrometer. Chemical shifts are reported in δ (ppm) relative to the solvent residual peak. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). HRMS was done on a Thermo Fisher Q Exactive LC/MS. Fluorescence spectra were measured using Shimadzu RF-5301PC. HPLC was carried out on Agilent 1200 LC with CH_3CN/H_2O (0.1% TFA) as eluents.

2. Synthesis and characterization of PQ derivatives and N-vinyl compounds

1-(9,10-dioxo-6-(4-(trifluoromethyl)phenyl)-9,10-dihydrophenanthren-3-yl)-1-oxo-5,8,11-trioxa-2-azatetradecan-14-oic acid (PQ1-PEG$_3$-COOH)



3-chloro-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde (1a)

4-bromo-2-chlorobenzaldehyde(6.6g, 30mmol, 1.0eq), (4-(trifluoromethyl)phenyl)boronic acid (11.4g, 60 mmol, 2.0eq), $Pd(PPh_3)_4$ (1.04g, 3mol%) and K_2CO_3 (8.3g, 60mmol, 2.0eq) was taken in a two neck round bottomed flask. 300 mL DMF was added to it and the reaction mixture was degassed properly with N_2. Next the reaction was allowed to stir at 80 °C for overnight. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature. It was diluted with water and extracted with ethyl acetate several times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Products were purified by silica gel column chromatography to give the product **1a** (White solid , 5.6g, 65% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.51 (d, *J* = 0.8 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.67 (m, 5H), 7.61 (ddd, *J* = 8.1, 1.8, 0.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.2, 146.5, 141.8, 138.5, 131.7, 131.1, 130.8, 130.0, 129.2, 127.6, 126.1, 126.1, 126.1, 126.0. m/z: $[M+H]^+$ calcd:285.0289; found:285.0280.

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde (1b)

1a (1.4g, 5mmol, 1.0eq), $[Pd(dppf)Cl_2]$ (0.11g, 3mol%), XPhos (0.143g, 6mol%), B_2Pin (2.54g. 10mmol, 2.0eq) and KOAc(1.47g, 15mmol, 3.0eq) was taken in a three neck round bottomed flask. The reaction mixture was degassed properly with N_2. Then 100ml MeCN was added and the reaction was refluxed to stir at 80 °C for overnight. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was

cooled to room temperature. It was diluted with water and extracted with ethyl acetate several times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Products were purified by silica gel column chromatography to give the product **1b** (White solid , 1.5g, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.61 (d, *J* = 0.6 Hz, 1H), 8.10 – 8.04 (m, 2H), 7.79 – 7.69 (m, 5H), 1.41 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.1, 144.0, 143.4, 140.8, 134.5, 129.5, 128.5, 127.8, 125.8 (q, *J* = 3.7 Hz), 84.6, 83.5, 25.0, 24.9. m/z: $[M+H]^+$ calcd:377.1530; found:377.1527.

Methyl 3-bromo-4-formylbenzoate (1c)

3-bromo-4-formylbenzoic acid (5g, 21.9mmol, 1.0eq) was added to in a round bottomed flask, followed by 100ml DMF, potassium carbonate (6.05g, 43.8mmol,2.0eq) and methyl iodide (3ml, 48.2mmol, 1.1eq). The reaction was stirred at room temperature overnight. The reaction was monitored by TLC. After completion of the reaction, it was diluted with water and extracted with ethyl acetate several times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Products were purified by silica gel column chromatography to give the product **1c** (White solid , 4.7g, 88% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 10.40 (d, *J* = 0.9 Hz, 1H), 8.31 (d, *J* = 1.6 Hz, 1H), 8.05 (ddd, *J* = 8.1, 1.6, 0.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 191.2, 164.8, 136. 2, 136.0, 135.0, 129.7, 128.7, 126.6, 52.8. m/z: $[M]^-$ calcd:241.9573; found:241.9583.

Methyl 9,10-dioxo-6-(4-(trifluoromethyl)phenyl)-9,10-dihydrophenanthrene-3-carboxylate (PQ1)[1]

1b (2.0g, 5.3 mmol, 1.2eq), **1c** (1.1g, 4.4mmol, 1.0eq), $Pd(PPh_3)_2Cl_2$ (0.7g, 10 mol%) and K_3PO_4 (1.4g, 6.6mmol,1.5 eq) was taken in a two neck round bottomed flask. 50 mL DMSO was added to it and the reaction mixture was degassed properly with N_2. Next the reaction was allowed to stir at 90 ^{o}C for 6 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and added CuCl (0.044g, 10 mol %) and TBHP (3.6ml, 26.4mmol, 6.0 eq). It was stirred for another 3 h at rt. Then it was diluted with water and extracted with ethyl acetate several times. The organic parts were collected together and concentrated under vacuum after drying over Na_2SO_4. Products were purified by silica gel column chromatography to give the product **PQ1** (Yellow Solid, 260mg, 15% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.74 (d, *J* = 1.4 Hz, 1H), 8.31 – 8.25 (m, 3H), 8.12 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.82 (d, *J* = 1.5 Hz, 4H), 7.71 (dd, *J* = 8.1, 1.6 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 179.8, 179.2, 165.6, 147.6, 142.7, 136.4, 135.6, 135.6, 133.6, 131.5, 130.7, 130.3, 130.3, 128.9, 127.8, 126. 2, 125.3, 123.2, 52.9. m/z: $[M+H]^+$ calcd:411.0839; found:411.0839.

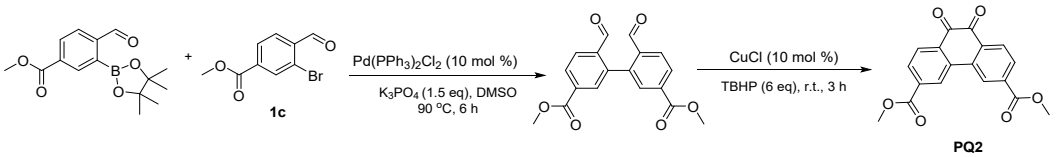
9,10-dioxo-6-(4-(trifluoromethyl)phenyl)-9,10-dihydrophenanthrene-3-carboxylic acid (1d)

PQ1 (40mg, 0.097mmol) was dissolved in tetrahydrofuran (10 mL) in a round bottomed flask, followed by aqueous lithium hydroxide (10 mL, 1 M). The reaction was stirred at room temperature for 2h. The reaction was monitored by TLC. After completion of the reaction, the mixture was acidified with 1 M aqueous hydrochloric acid to pH = 7 and extracted with diethyl ether twice (2 x 10 mL). The combined organic layers were dried over sodium sulfate and concentrated in vacuo. The reaction mixture was purified by prep HPLC to give the product **1d** (yellow solid,18.6mg, 48% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (d, *J* = 1.5 Hz, 1H), 8.56 (d, *J* = 1.7 Hz, 1H), 8.21 – 8.09 (m, 4H), 8.05 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.91 (dd, *J* = 8.1, 1.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.4, 178.0, 166.6, 145.1, 142.7, 136.3, 135.2, 135.1, 134.3, 131.0, 130.0, 129.7, 129.3, 129.1, 128.8, 128.4, 128.3, 125.8, 125.4, 123.2. m/z: $[M+H]^+$ calcd:397.0678; found:397.0672.

1-(9,10-dioxo-6-(4-(trifluoromethyl)phenyl)-9,10-dihydrophenanthren-3-yl)-1-oxo-5,8,11-trioxa-2-azatetradecan-14-oic acid (PQ1-PEG$_3$-COOH)

Compound **1e** (30 mg, 0.076 mmol,1.0eq) , DCC (47.5 mg, 0.23 mmol, 3.0eq), NHS (26.5mg, 0.23 mmol, 3.0eq) were dissolved in 5 mL THF in a round bottomed flask and stirred at room temperature for 4 h. The reaction was monitored by TLC. Then, DIPEA (26μL, 0.15mmol, 2.0eq) and NH_2-PEG_3-COOH (50.9 mg, 0.23 mmol, 3.0eq) were added. The mixture was stirred at room temperature for 12 hours and was monitored by TLC. After the reaction was finished, the reaction mixture was purified by prep HPLC to give the product **PQ1-PEG$_3$-COOH** (yellow solid, 15mg, 33% yield). ^{1}H NMR (500 MHz, DMSO-d6) δ 8.93 (t, *J* = 5.6 Hz, 1H), 8.78 (d, *J* = 1.6 Hz, 1H), 8.62 (d, *J* = 1.7 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.13 (dd, *J* = 8.1, 2.8 Hz, 3H), 7.97 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.92 (dd, *J* = 8.1, 1.7 Hz, 1H), 3.62 – 3.43 (m, 16H). ^{13}C NMR (126 MHz, DMSO-d6) δ 178.5, 178.3, 172.6, 165.3, 145.2, 142.9, 139.9, 135.5, 135.0, 133.1, 131.1, 130.0, 129.2, 128.3, 128.2, 126.0, 123.4, 123.1, 69.7, 69.7, 69.6, 68.9, 66.2, 34.7.m/z: $[M+Na]^+$ calcd:622.1659; found:622.1649.

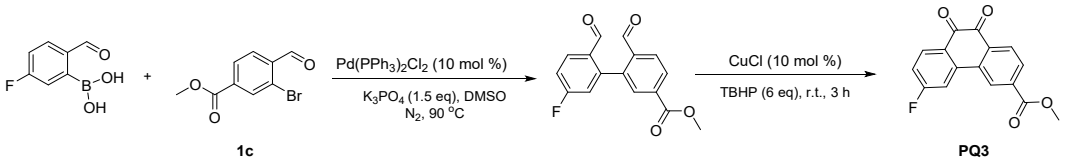
Dimethyl 9,10-dioxo-9,10-dihydrophenanthrene-3,6-dicarboxylate (PQ2)[1]



Methyl 4-formyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (2.01g, 7.2 mmol, 1.2eq), **1c** (1.46g, 6mmol, 1.0eq), $Pd(PPh3)_2Cl_2$ (0.42g, 10 mol%) and K_3PO_4 (1.92g, 9mmol,1.5 eq) was taken in a two neck round bottomed flask. 50 mL DMSO was added to it and the reaction mixture was degassed properly with N_2. Next the reaction was allowed to stir at 90 °C for 6 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and to it were added CuCl (0.060g, 10 mol %) and TBHP (5ml, 36mmol, 6.0 eq). It was

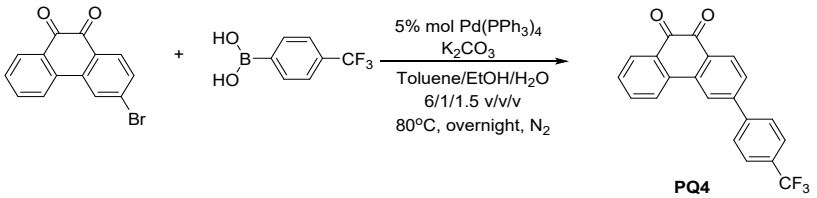
stirred for another 3 h at rt. Then it was diluted with water and extracted with ethyl acetate several times. The organic parts were collected together and concentrated under vacuum after drying over Na_2SO_4. Products were purified by silica gel column chromatography to give the product **PQ2** (Yellow Solid, 480mg, 25% yield) ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (d, J = 1.5 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 8.09 (dd, J = 8.0, 1.4 Hz, 2H), 3.97 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.9, 165.9, 135.2, 134.9, 130.2, 129.9, 125.0, 53.3. m/z: $[M+Na]^+$ calcd:347.0526; found:347.0520.

Methyl 6-fluoro-9,10-dioxo-9,10-dihydrophenanthrene-3-carboxylate (PQ3)[1]



(5-fluoro-2-formylphenyl)boronic acid (1.46g, 6 mmol, 1.2eq), **1c** (0.84g, 5mmol, 1.0eq), $Pd(PPh_3)_2Cl_2$ (0.35g, 10 mol%) and K_3PO_4 (1.6g, 7.5mmol,1.5 eq) was taken in a two neck round bottomed flask. 50 mL DMSO was added to it and the reaction mixture was degassed properly with N_2. Next the reaction was allowed to stir at 90 °C for 6 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and to it were added CuCl (0.05g, 10 mol %) and TBHP (2.88ml, 30mmol, 6.0 eq). It was stirred for another 3 h at rt. Then it was diluted with water and extracted with ethyl acetate several times. The organic parts were collected together and concentrated under vacuum after drying over Na_2SO_4. Products were purified by silica gel column chromatography to give the product **PQ3** (Yellow Solid, 100mg, 7% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (t, J = 3.0 Hz, 1H), 8.27 (t, J = 3.0 Hz, 1H), 8.15 (dd, J = 8.1, 1.4 Hz, 1H), 7.81 (dd, J = 10.1, 2.4 Hz, 1H), 7.21 (ddd, J = 8.7, 7.6, 2.3 Hz, 1H), 4.03 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.5, 178.0, 169.1, 166.5, 165.4, 138.2, 138.1, 136.4, 134.7, 134.7, 134.1, 134.0, 133.6, 130.7, 130.6, 127.8, 127.7, 125.5, 117.6, 117.4, 111.6, 111.4, 52.9. m/z: $[M+Na]^+$ calcd:307.0377; found:307.0370.

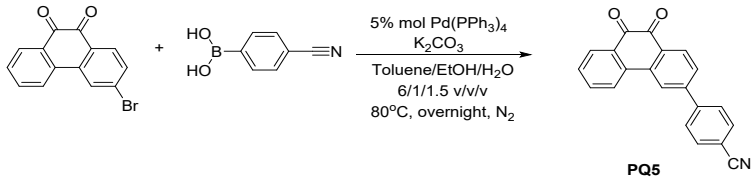
3-(4-(trifluoromethyl)phenyl)phenanthrene-9,10-dione (PQ4)[2]



3-bromophenanthrene-9,10-dione (1.44g, 5mmol, 1.0eq), (4-(trifluoromethyl)phenyl)boronic acid (1.9g, 10 mmol, 2.0eq) and $Pd(PPh_3)_4$ (0.29g, 5mol%) was taken in a two neck round bottomed flask and was degassed properly with N_2. Following the addition of K_2CO_3 solution (2.07g ,15mmol, 3.0eq in 7 mL H_2O), ethanol (5 ml), and toluene (28 mL), the reaction was allowed to stir at 80 °C for 12 h. After being cooled to room temperature, the

reaction mixture was diluted with dichloromethane, the phases were separated and the organic layer was washed with water and dried over anhydrous Na_2SO_4. Upon removal of solvents in vacuo, the residual was purified by silica gel column chromatography to give the product **PQ4** (yellow solid, 0.8g, 45%yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 – 8.15 (m, 3H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.85 – 7.73 (m, 5H), 7.68 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.51 (q, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 143.0, 136.5, 136.1, 135.5, 131.4, 131.3, 130.7, 130.0, 128.4, 127.7, 124.0, 123.0, 115.5.

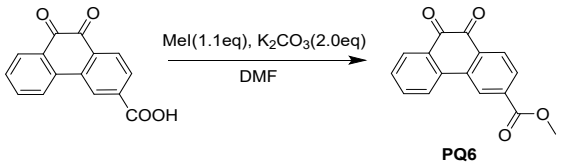
4-(9,10-dioxo-9,10-dihydrophenanthren-3-yl)benzonitrile (PQ5)[2]



PQ5

3-bromophenanthrene-9,10-dione (1.44g, 5mmol, 1.0eq), (4- cyanophenyl)boronic acid (1.1g, 7.5 mmol, 1.5eq) and $Pd(PPh_3)_4$ (0.29g, 5mol%) was taken in a two neck round bottomed flask and was degassed properly with N_2. Following the addition of K_2CO_3 solution (2.07g ,15mmol, 3.0eq in 7 mL H_2O), ethanol (5 ml), and toluene (28 mL), the reaction was allowed to stir at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane, the phases were separated and the organic layer was washed with water and dried over anhydrous Na_2SO_4. Upon removal of solvents in vacuo, the residual was purified by silica gel column chromatography to give the product **PQ5** (yellow solid, 0.13g, 9% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 8.1 Hz, 1H), 8.24 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.20 (d, *J* = 1.7 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.74 (m, 5H), 7.68 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.53 (td, *J* = 7.6, 1.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.1, 135.3, 132.9, 131.4, 130.8, 130.1, 128.3, 128.1, 124.0, 123.0.

Methyl 9,10-dioxo-9,10-dihydrophenanthrene-3-carboxylate (PQ6)

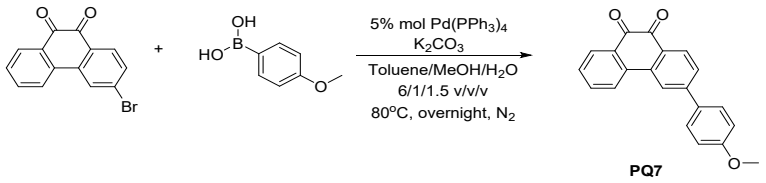


PQ6

9,10-dioxo-9,10-dihydrophenanthrene-3-carboxylic acid (1g, 4mmol, 1.0eq) was added to in a round bottomed flask, followed by 30ml DMF, potassium carbonate (1.1g, 8mmol, 2.0eq) and methyl iodide (0.27ml, 4.4mmol, 1.1eq). The reaction was stirred at room temperature overnight. The reaction was monitored by TLC. After completion of the reaction, it was diluted with water and extracted with ethyl acetate several times. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Products were purified by silica gel column

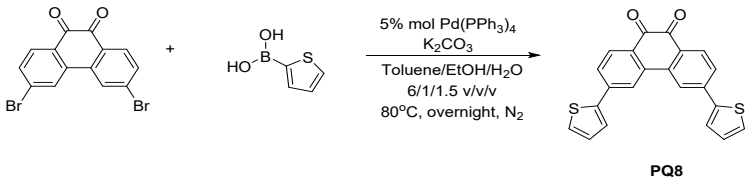
chromatography to give the product **PQ6** (Yellow solid , 0.5g, 47% yield) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 1.5 Hz, 1H), 8.28 – 8.21 (m, 2H), 8.12 (ddd, *J* = 22.1, 8.1, 1.3 Hz, 2H), 7.82 – 7.74 (m, 1H), 7.53 (td, *J* = 7.6, 1.1 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 180.0, 179.6, 165.6, 136.3, 136.2, 136.0, 135.0, 133.3, 130.9, 130.7, 130.5, 130.1, 129.9, 125.4, 124.3, 52.9. m/z: $[M+Na]^+$ calcd:289.0471; found:289.0464.

3-(4-methoxyphenyl)phenanthrene-9,10-dione (PQ7)[2]



3-bromophenanthrene-9,10-dione (1.44g, 5mmol, 1.0eq), (4- methoxyphenyl)boronic acid (1.14g, 7.5 mmol, 1.5eq) and $Pd(PPh_3)_4$ (0.29g, 5mol%) was taken in a two neck round bottomed flask and was degassed properly with N_2. Following the addition of K_2CO_3 solution (2.07g ,15mmol, 3.0eq in 7 mL H_2O), methanol (5 ml), and toluene (28 mL), the reaction was allowed to stir at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane, the phases were separated and the organic layer was washed with water and dried over anhydrous Na_2SO_4. Upon removal of solvents in vacuo, the residual was purified by silica gel column chromatography to give the product **PQ7** (yellow solid, 1.3g, 83% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.17 (m, 2H), 8.15 (d, *J* = 1.8 Hz, 1H)8.10 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.67 – 7.64 (m, 2H), 7.62 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.48 (td, *J* = 7.6, 1.1 Hz, 1H), 7.06 – 7.03 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.6, 179.8, 160.6, 148.4, 136.2, 135.9, 135.9, 131.8, 131.3, 131.2, 130.5, 129.6, 129.3, 128.5, 127.6, 123.9, 122.0, 116.1, 114.8, 114.7, 55.5.

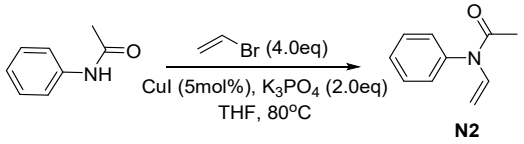
3,6-di(thiophen-2-yl)phenanthrene-9,10-dione (PQ8)[3]



3,6-dibromophenanthrene-9,10-dione (1.83g, 5 mmol,1.0eq), and 2-thienylboronic acid (2.55g,12.5 mmol, 2.5eq), and $Pd(PPh_3)_4$ (0.29g, 5mol%) was taken in a two neck round bottomed flask and was degassed properly with N_2. Following the addition of K_2CO_3 solution (2.07g ,15mmol, 3.0eq in 7 mL H_2O), ethanol (5 ml), and toluene (28 mL), the reaction was allowed to stir at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane, the phases were separated and the organic layer was washed with water and dried over anhydrous Na_2SO_4. Upon removal of solvents in vacuo, the residual was purified by silica gel

column chromatography to obtain **PQ8** (Orange solid, 0.39g, 22% yield).^{1}H NMR (400 MHz, DMSO-d_6) δ 8.63 (d, J = 1.8 Hz, 2H), 8.12 – 8.02 (m, 4H), 7.82 – 7.74 (m, 4H), 7.29 (dd, J = 5.0, 3.7 Hz, 2H).^{13}C NMR (101 MHz, DMSO-d_6) δ 178.8, 142.2, 140.7, 136.2, 130.9, 130.6, 129.5, 129.0, 127.7, 126.8, 121.3.

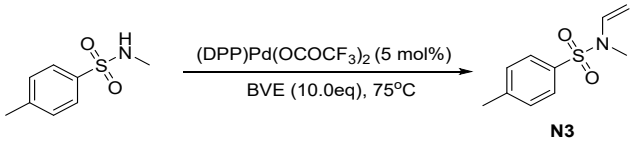
N2[4]



N2

Acetanilide (1.35g, 10 mmol, 1.0eq), CuI (95.2 mg, 0.50 mmol, 0.05eq), K_3PO_4 (4.25 g, 20 mmol, 2.0eq) and vinyl bromide (1 M in THF, 40 mL, 40 mmol, 4.0eq) were added in a round bottomed flask. The reaction mixture was stirred for 24h at 80 ºC, then filtered through a Celite pad, which was washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to give the product **N2** (colorless solid, 1.1g, 70%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 – 7.63 (m, 1H), 7.55 – 7.42 (m, 3H), 7.24 – 7.14 (m, 2H), 4.39 (d, J = 9.0 Hz, 1H), 3.86 (d, J = 15.9 Hz, 1H), 1.88 (s, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 168.8, 133.7, 130.0, 128.9, 128.7, 124.0, 119.8, 96.3, 23.2.

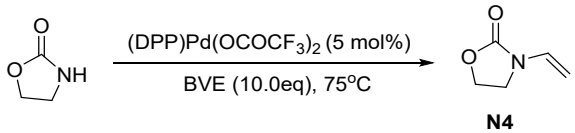
N3[5]



N3

N,4-dimethylbenzenesulfonamide(1.85g, 10 mmol, 1.0eq), BVE (13ml, 100 mmol, 10.0eq), and (DPP)Pd(OCOCF$_3$)$_2$ (0.34g, 0.5 mmol, 0.05eq) were added in a round bottom flask. The flask was capped by a rubber septum with an 18 gauge needle punctured through it. The reaction was stirred at 75 °C in an oil bath and monitored for completion by TLC. Upon completion, the reaction mixture was allowed to cool and loaded directly onto a silica gel column chromatography to give the product **N3** (colorless solid, 1.2g, 50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 2H), 7.34 – 7.27 (m, 2H), 7.00 (dd, J = 15.6, 9.1 Hz, 1H), 4.32 (dd, J = 9.0, 1.4 Hz, 1H), 4.18 (dd, J = 15.6, 1.4 Hz, 1H), 2.86 (s, 3H), 2.42 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 134.8, 133.8, 129.7, 127.0, 93.1, 31.2, 21.5.

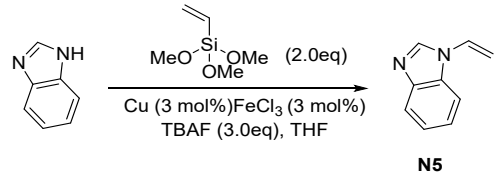
N4[5]



N4

Oxazolidin-2-one (0.87g, 10 mmol, 1.0eq), BVE (13ml, 100 mmol, 10.0eq), and (DPP)Pd($OCOCF_3$)$_2$ (0.34g, 0.5 mmol, 0.05eq) were combined in a round bottom flask. The flask was capped by a rubber septum with an 18 gauge needle punctured through it. The reaction was stirred at 75 °C in an oil bath and monitored for completion by TLC. Upon completion, the reaction mixture was allowed to cool and loaded directly onto a silica gel column chromatography to give the product **N4** (colorless oil, 1.0g, 90%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (dd, *J* = 15.8, 8.9 Hz, 1H), 4.47 – 4.39 (m, 3H), 4.28 (dd, *J* = 15.8, 1.3 Hz, 1H), 3.75 – 3.66 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.3, 129.8, 93.4, 62.1, 41.8.

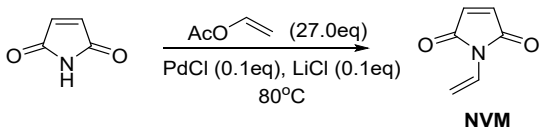
N5[6]



N5

1H-benzo[d]imidazole (0.35g, 3mmol, 1.0eq), trimethoxy(vinyl)silane (0.89g, 6mmol, 2.0eq), Cu (6mg, 3 mol%), $FeCl_3$ (15mg, 3 mol%), and TBAF in THF (2.4ml, 9 mmol, 3.0eq) were added in a round bottom flask and stirred in air atmosphere at room temperature for overnight. After the reaction was finished, the mixture was poured into ethyl acetate, washed with saturated brine, extracted with ethyl acetate, dried over anhydrous Na_2SO_4 and evaporated under vacuum, the residue was purified by silica gel column chromatography to give the product **N5** (Pale yellow oil, 95mg, 22% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.13 (s, 1H), 7.81 (dd, J = 6.8, 2.2 Hz, 1H), 7.57 – 7.47 (m, 1H), 7.31 (tt, J = 7.3, 5.8 Hz, 2H), 7.09 (dd, J = 15.9, 9.0 Hz, 1H), 5.49 (dd, J = 15.9, 1.7 Hz, 1H), 5.05 (dd, J = 9.0, 1.7 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-d) δ 128.0, 123.8, 123.0, 120.5, 110.3, 102.5.

NVM[7]

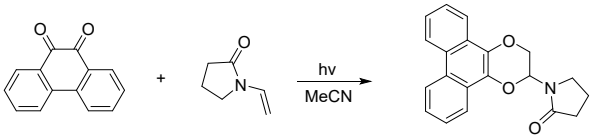


NVM

Maleimide (1.30 g, 13.4 mmol, 1.0 eq), palladium(II) chloride (240 mg, 1.34 mmol, 0.1 eq), lithium chloride (57.0 mg, 1.34 mmol, 0.1 eq) and vinyl acetate (33.2 mL, 359 mmol, 27.0 eq) were added in a round bottom flask. After stirring at 80 °C for 20 h, the resulting mixture was cooled down to room temperature. Purification by silica gel column chromatography to give the product **NVM** (bright yellow solid., 1.1g, 69%) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.11 (s, 1H), 6.62 (dd, *J* = 16.3, 9.8 Hz, 1H), 5.70 (d, *J* = 16.3 Hz, 1H), 4.91 (d, *J* = 9.8 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 134.9, 123.5, 102.1.

3. Preparation and characterization of the DVPC 2.0 products

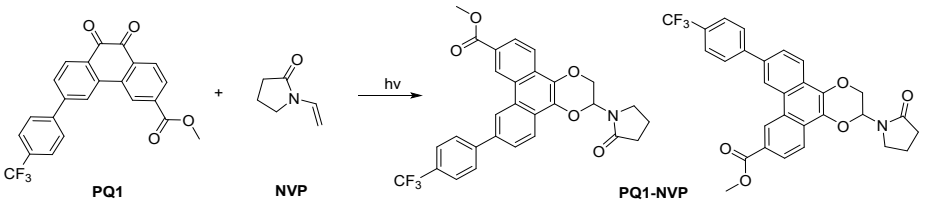
General preparation procedure: PQ or PQ derivatives (0.5 mmol) and N-vinyl compounds (2.5 mmol) were dissolved in CH3CN (30 mL). Then the mixture was stirred and irradiated by the white light LED lamp. The reaction was monitored by TLC. The product was purified by prep-HPLC. White solid was obtained.



PQ NVP PQ-NVP

PQ-NVP

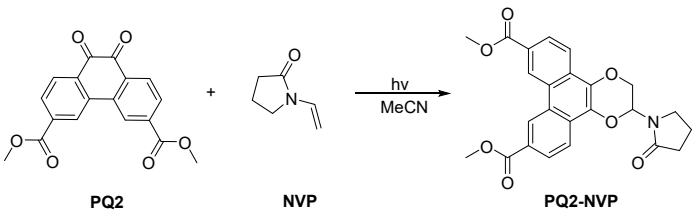
^{1}H NMR (400 MHz, Chloroform-d) δ 8.61 (dd, *J* = 7.9, 1.6 Hz, 2H), 8.21 – 8.12 (m, 2H), 7.65 – 7.55 (m, 4H), 6.32 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.54 (dd, *J* = 11.2, 2.6 Hz, 1H), 4.45 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.68 – 3.58 (m, 2H), 2.54 (t, *J* = 8.2 Hz, 2H), 2.09 (p, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.6, 132.7, 127.0, 126.8, 126.8, 126.7, 125.8, 125.7, 125.4, 125.3, 122.5, 120.8, 120.8, 75.2, 65.7, 43.8, 30.9, 18.3. m/z :[M+H]$^+$calcd:320.1286; found:320.1277.



PQ1 NVP PQ1-NVP

PQ1-NVP

^{1}H NMR (400 MHz, Chloroform-d) δ 9.38 (d, *J* = 1.8 Hz, 1H), 8.87 (d, *J* = 1.7 Hz, 1H), 8.29 – 8.19 (m, 3H), 7.92 – 7.85 (m, 3H), 7.79 (d, *J* = 8.2 Hz, 2H), 6.34 (ddd, *J* = 12.0, 5.8, 2.6 Hz, 1H), 4.60 (ddd, *J* = 11.2, 5.9, 2.7 Hz, 1H), 4.48 (ddd, *J* = 11.2, 5.8, 4.4 Hz, 1H), 4.04 (s, 3H), 3.65 (d, *J* = 13.3 Hz, 2H), 2.57 (d, *J* = 16.5 Hz, 2H), 2.18 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.7, 167.4, 144.6, 137.4, 137.3, 134.8, 132.9, 129.1, 127.9, 127.6, 127.4, 127.2, 127.1, 126.8, 126.7, 126.6, 126.5, 126.1, 125.9, 125.9, 125.5, 124.9, 121.9, 121.9, 121.5, 121.2, 75.3, 75.2, 65.7, 65.6, 52.4, 43.6, 30.8, 18.3. [M+Na]$^+$ calcd:544.1348; found:544.1340.

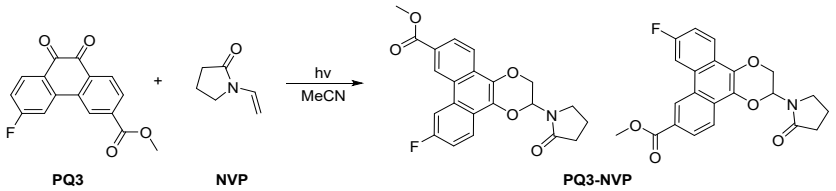


PQ2 NVP PQ2-NVP

PQ2-NVP

^{1}H NMR (400 MHz, Chloroform-d) δ 9.41 (d, *J* = 1.5 Hz, 2H), 8.30 – 8.17 (m, 4H), 6.32 (dd, *J* = 6.1, 2.6 Hz, 1H), 4.60 (dd, *J* = 11.2, 2.7 Hz, 1H), 4.47 (dd, *J* = 11.2, 6.1 Hz, 1H), 4.05 (s, 6H), 3.70 – 3.57 (m, 2H), 2.55 (dd, *J* = 8.8,

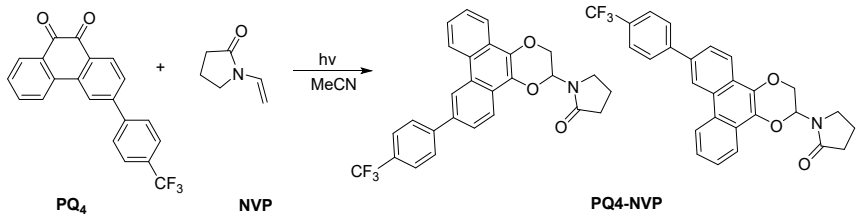
7.5 Hz, 2H), 2.18 – 2.10 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.4, 167.2, 134.6, 134.4, 128.8, 127.4, 127.3, 127.2, 126.7, 126.5, 125.1, 121.3, 121.2, 75.3, 65.7, 52.4, 43.5, 30.8, 18.3. m/z: $[M-H]^-$ calcd:434.1240; found:434.1245.



PQ3 **NVP** **PQ3-NVP**

PQ3-NVP

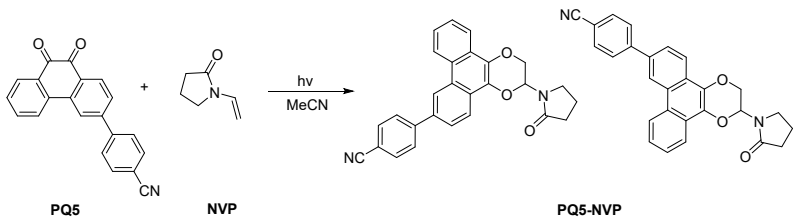
^{1}H NMR (400 MHz, Chloroform-d) δ 9.52 (d, *J* = 1.6 Hz, 1H), 8.65 (dd, *J* = 10.9, 2.5 Hz, 1H), 8.57 (ddd, *J* = 8.6, 5.6, 1.5 Hz, 1H), 8.54 – 8.46 (m, 2H), 7.73 (dddd, *J* = 9.0, 7.9, 4.1, 2.5 Hz, 1H), 6.64 (ddd, *J* = 15.1, 5.8, 2.6 Hz, 1H), 4.90 (ddd, *J* = 11.2, 6.2, 2.6 Hz, 1H), 4.79 (dt, *J* = 11.4, 5.7 Hz, 1H), 4.36 (s, 3H), 4.05 – 3.92 (m, 2H), 2.90 (td, *J* = 8.1, 2.6 Hz, 2H), 2.52 – 2.42 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.9, 167.2, 131.9, 129.3, 129.0, 127.4, 127.3, 126.7, 126.6, 125.2, 121.1, 121.1, 116.4, 116.3, 116.1, 108.2, 108.0, 75.4, 75.1, 65.7, 65.5, 52.3, 43.7, 30.8, 30.8, 18.3. $[M+Na]^+$ calcd:418.1067; found:418.1059.



PQ_4 **NVP** **PQ4-NVP**

PQ4-NVP

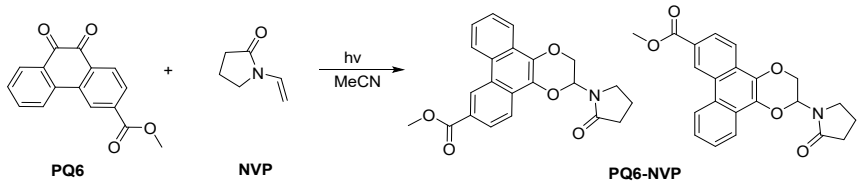
^{1}H NMR (400 MHz, Chloroform-d) δ 8.80 (d, *J* = 1.7 Hz, 1H), 8.71 – 8.66 (m, 1H), 8.25 (dd, *J* = 8.5, 2.2 Hz, 1H), 8.19 (dt, *J* = 7.9, 2.2 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.68 – 7.59 (m, 2H), 6.34 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.57 (dd, *J* = 11.2, 2.6 Hz, 1H), 4.48 (ddd, *J* = 11.1, 5.4, 2.1 Hz, 1H), 3.70 – 3.61 (m, 2H), 2.58 (d, *J* = 8.1 Hz, 2H), 2.12 (q, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.9, 144.9, 136.7, 136.6, 127.7, 127.3, 127.2, 127.2, 127.0, 127.0, 126.8, 126.2, 126.0, 125.9, 125.9, 125.8, 125.6, 125.5, 125.5, 125.3, 122.5, 121.7, 121.7, 121.3, 121.0, 121.0, 75.3, 75.2, 65.7, 65.7, 43.8, 43.8, 30.9, 18.3. $[M+Na]^+$ calcd:486.1293; found:486.1285.



PQ5 **NVP** **PQ5-NVP**

PQ5-NVP

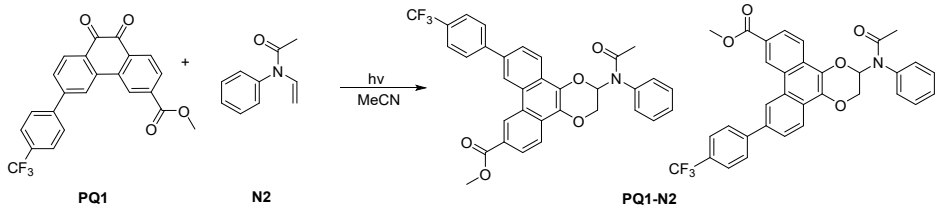
^{1}H NMR (400 MHz, Chloroform-d) δ 8.80 (d, *J* = 1.8 Hz, 1H), 8.67 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.22 – 8.16 (m, 1H), 7.89 – 7.78 (m, 5H), 7.68 – 7.60 (m, 2H), 6.34 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.58 (ddd, *J* = 11.2, 2.7, 1.5 Hz, 1H), 4.48 (ddd, *J* = 11.2, 5.5, 3.9 Hz, 1H), 3.71 – 3.61 (m, 2H), 2.58 (t, *J* = 8.2 Hz, 2H), 2.17 – 2.08 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.1, 145.9, 136.0, 135.9, 133.5, 132.7, 132.5, 128.0, 127.3, 127.3, 127.1, 127.0, 126.7, 126.2, 126.0, 125.8, 125.7, 125.7, 125.6, 122.4, 121.9, 121.8, 121.4, 121.1, 119.0, 110.9, 75.3, 75.2, 65.7, 65.6, 43.9, 43.9, 30.8, 18.3. $[M+Na]^{+}$ calcd:443.1372; found:443.1363.



PQ6 NVP PQ6-NVP

PQ6-NVP

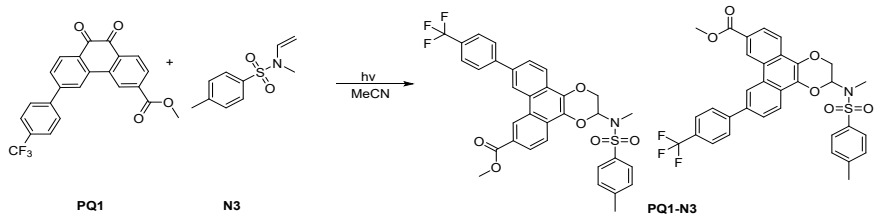
^{1}H NMR (400 MHz, DMSO-d6) δ 9.31 (s, 1H), 8.82 (d, *J* = 7.5 Hz, 1H), 8.25 – 8.06 (m, 3H), 7.80 – 7.63 (m, 2H), 6.10 (ddd, *J* = 13.3, 6.8, 2.6 Hz, 1H), 4.71 (ddd, *J* = 11.2, 8.3, 2.7 Hz, 1H), 4.58 (ddd, *J* = 11.5, 9.2, 6.8 Hz, 1H), 3.96 (s, 3H), 2.41 (t, *J* = 8.0 Hz, 2H), 2.02 (p, *J* = 8.5, 7.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.9, 167.4, 134.9, 134.8, 132.4, 128.7, 128.6, 127.4, 127.3, 127.3, 127.3, 127.0, 126.8, 126.7, 126.6, 126.5, 126.4, 126.1, 126.0, 125.9, 125.9, 125.8, 125.0, 122.7, 120.0, 121.0, 121.0, 120.9, 75.3, 65.6, 65.5, 52.3, 43.8, 30.8, 18.2. $[M+Na]^{+}$ calcd:400.1161; found:400.1153.



PQ1 N2 PQ1-N2

PQ1-N2

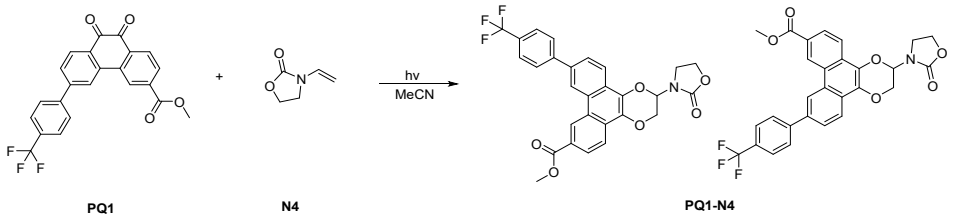
^{1}H NMR (500 MHz, Chloroform-d) δ 9.32 (dd, *J* = 7.3, 1.5 Hz, 1H), 8.81 (dd, *J* = 7.2, 1.8 Hz, 1H), 8.34 – 8.16 (m, 2H), 8.12 (dd, *J* = 26.3, 8.5 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.82 – 7.75 (m, 3H), 7.53 (d, *J* = 33.6 Hz, 1H), 7.40 (dq, *J* = 13.2, 7.3, 6.2 Hz, 4H), 6.86 (t, *J* = 11.3 Hz, 1H), 4.58 (ddd, *J* = 10.9, 5.9, 2.5 Hz, 1H), 4.02 (d, *J* = 12.6 Hz, 3H), 3.84 (ddd, *J* = 13.9, 10.9, 8.2 Hz, 1H), 1.99 (s, 3H).^{13}C NMR (126 MHz, Chloroform-d) δ 171.9, 167.4, 167.4, 144.7, 137.7, 137.1, 137.0, 134.7, 134.4, 132.6, 129.3, 129.3, 129.1, 127.8, 127.8, 127.4, 127.2, 127.0, 126.6, 126.5, 126.4, 126.2, 125.9, 125.8, 125.8, 125.6, 124.8, 124.8, 121.9, 121.8, 121.4, 121.3, 121.2, 121.1, 65.9, 65.8, 52.3, 52.3, 23.2. m/z: $[M+Na]^{+}$ calcd:594.1505; found:594.1498.



PQ1 N3 PQ1-N3

PQ1-N3

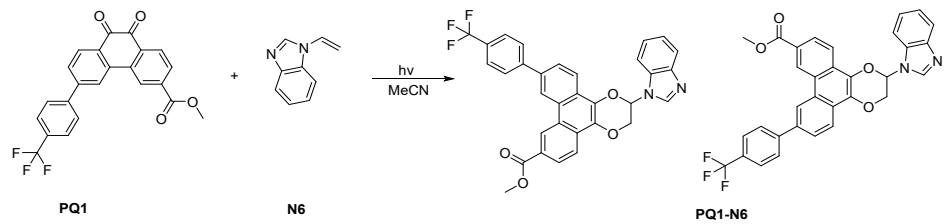
^{1}H NMR (400 MHz, Chloroform-d) δ 9.34 (t, *J* = 2.0 Hz, 1H), 8.83 (d, *J* = 1.7 Hz, 1H), 8.27 – 8.18 (m, 2H), 8.07 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.94 – 7.85 (m, 5H), 7.79 (dd, *J* = 8.3, 3.7 Hz, 2H), 7.69 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 6.25 (ddd, *J* = 8.7, 7.8, 2.8 Hz, 1H), 4.69 (ddd, *J* = 10.6, 7.5, 2.8 Hz, 1H), 4.33 (ddd, *J* = 11.0, 7.8, 6.2 Hz, 1H), 4.03 (d, *J* = 5.4 Hz, 3H), 3.00 (s, 3H), 2.56 (d, *J* = 5.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.3, 167.3, 144.4, 144.2, 137.4, 137.3, 135.5, 135.5, 134.4, 132.7, 132.6, 129.9, 128.9, 128.1, 127.9, 127.2, 126.8, 126.7, 126.3, 126.0, 125.9, 125.9, 124.9, 124.9, 121.9, 121.6, 121.5, 121.4, 121.2, 120.8, 80.7, 80.5, 65.9, 65.8, 52.4, 52.4, 29.7, 29.6 , 21.7. m/z: $[M]^+$ calcd:621.1433; found:621.1431.



PQ1 N4 PQ1-N4

PQ1-N4

^{1}H NMR (400 MHz, Chloroform-d) δ 9.38 (d, *J* = 1.6 Hz, 1H), 8.87 (d, *J* = 1.8 Hz, 1H), 8.31 – 8.19 (m, 3H), 7.92 – 7.86 (m, 3H), 7.79 (d, *J* = 8.2 Hz, 2H), 6.20 (ddd, *J* = 12.6, 5.2, 2.6 Hz, 1H), 4.66 (ddd, *J* = 11.4, 6.9, 2.6 Hz, 1H), 4.55 (ddd, *J* = 11.3, 5.2, 2.8 Hz, 1H), 4.47 – 4.41 (m, 2H), 4.03 (s, 3H), 3.88 – 3.80 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.3, 157.9, 137.6, 134.6, 132.9, 128.9, 127.9, 127.7, 127.4, 127.2, 127.2, 127.0, 126.9, 126.6, 126.5, 126.2, 125.9, 125.9, 125.5, 125.3, 124.9, 122.0, 121.9, 121.5, 121.3, 121.2, 65.9, 65.9, 62.7, 52.4, 41.3. m/z: $[M]^+$ calcd:523.1243; found:523.1238.

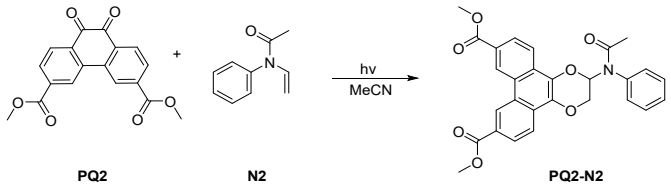


PQ1 N6 PQ1-N6

PQ1-N6

^{1}H NMR (500 MHz, Chloroform-d) δ 9.34 (d, *J* = 1.4 Hz, 2H), 8.83 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.33 – 8.11 (m, 3H), 7.95 (dd, *J* = 8.3, 4.7 Hz, 2H), 7.90 – 7.82 (m, 3H), 7.78 (dd, *J* = 8.2, 5.7 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.55 (t,

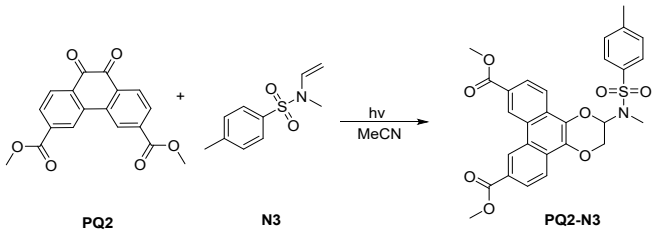
J = 7.8 Hz, 1H), 6.89 (s, 1H), 5.30 (t, *J* = 14.6 Hz, 1H), 4.98 (t, *J* = 10.8 Hz, 1H), 4.02 (d, *J* = 7.9 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-d) δ 167.0, 167.0, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.6, 127.5, 127.1, 127.0, 126.8, 126.8, 126.8, 126.6, 126.6, 125.9, 125.0, 124.9, 124.8, 124.6, 122.1, 121.7, 121.5, 121.4, 121.2, 120.6, 117.8, 117.7, 112.0, 111.9, 78.2, 78.0, 64.6, 64.6, 52.4. m/z: $[M+H]^+$ calcd:555.1531; found:555.1523.



PQ2 N2 PQ2-N2

PQ2-N2

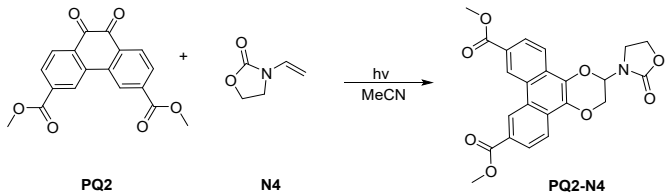
^{1}H NMR (400 MHz, Chloroform-d) δ 9.40 – 9.33 (m, 2H), 8.30 – 8.24 (m, 2H), 8.19 (dd, *J* = 8.6, 1.6 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.27 (m, 5H), 6.84 (d, *J* = 6.2 Hz, 1H), 4.58 (dd, *J* = 11.0, 2.5 Hz, 1H), 4.04 (d, *J* = 9.0 Hz, 6H), 3.85 (dd, *J* = 11.0, 8.1 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 171.8, 167.3, 167.3, 137.6, 134.4, 134.1, 129.3, 129.0, 128.8, 127.2, 127.0, 127.0, 126.5, 126.2, 125.0, 125.0, 121.1, 121.1, 65.8, 52.3, 52.3, 23.2. m/z: $[M-H]^-$ calcd:484.1397; found:484.1397.



PQ2 N3 PQ2-N3

PQ2-N3

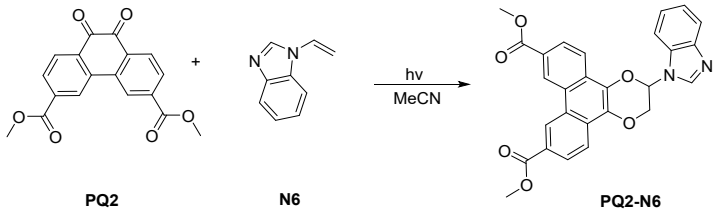
^{1}H NMR (400 MHz, Chloroform-d) δ 9.35 (s, 2H), 8.24 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.19 (d, *J* = 8.6 Hz, 1H), 8.07 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.42 (dd, *J* = 8.3, 5.1 Hz, 3H), 6.23 (dd, *J* = 7.9, 2.8 Hz, 1H), 4.69 (dd, *J* = 11.0, 2.8 Hz, 1H), 4.31 (dd, *J* = 11.0, 7.9 Hz, 1H), 4.04 (d, *J* = 4.7 Hz, 6H), 2.99 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.2, 167.1, 144.4, 135.4, 134.2, 134.1, 129.9, 128.8, 128.7, 128.1, 127.4, 127.3, 127.2, 126.9, 126.6, 126.4, 125.1, 125.0, 121.3, 120.8, 80.6, 65.8, 52.4,52.4, 29.7, 21.7. m/z: $[M-H]^-$ calcd:534.1223; found:534.1229.



PQ2 N4 PQ2-N4

PQ2-N4

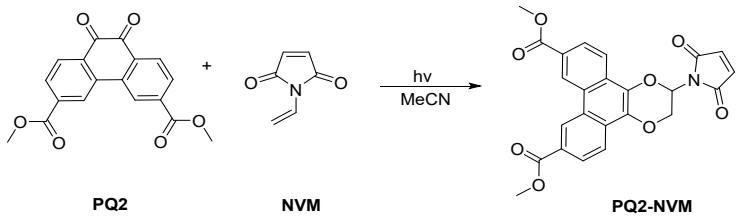
^{1}H NMR (400 MHz, Chloroform-d) δ 9.41 (d, *J* = 1.4 Hz, 2H), 8.28 – 8.19 (m, 4H), 6.18 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.65 (dd, *J* = 11.3, 2.7 Hz, 1H), 4.54 (dd, *J* = 11.3, 5.4 Hz, 1H), 4.47 – 4.41 (m, 2H), 4.05 (s, 6H), 3.85 – 3.79 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.2, 157.8, 134.4, 134.3, 128.7, 128.5, 127.5, 127.4, 127.4, 127.3, 126.7, 126.5, 125.1, 121.2, 121.1, 77.1, 65.8, 62.7, 52.4, 41.1. m/z: $[M-H]^-$ calcd:436.1033;found:436.1042.



PQ2 N6 PQ2-N6

PQ2-N6

^{1}H NMR (400 MHz, Chloroform-d) δ 9.36 – 9.22 (m, 3H), 8.22 (d, *J* = 1.1 Hz, 2H), 8.20 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.64 – 7.51 (m, 2H), 6.88 (t, *J* = 2.8 Hz, 1H), 5.27 (dd, *J* = 12.3, 3.3 Hz, 1H), 4.97 (dd, *J* = 12.2, 2.3 Hz, 1H), 4.03 (d, *J* = 4.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 166.9, 166.9, 139.7, 135.0, 134.3, 131.9, 131.3, 128.2, 128.1, 127.9, 127.7, 127.0, 126.7, 126.5, 125.1, 125.0, 121.4, 120.6, 117.9, 111.9, 78.1, 64.6, 52.5. m/z:$[M+H]^+$ calcd:469.1399; found:469.1390.



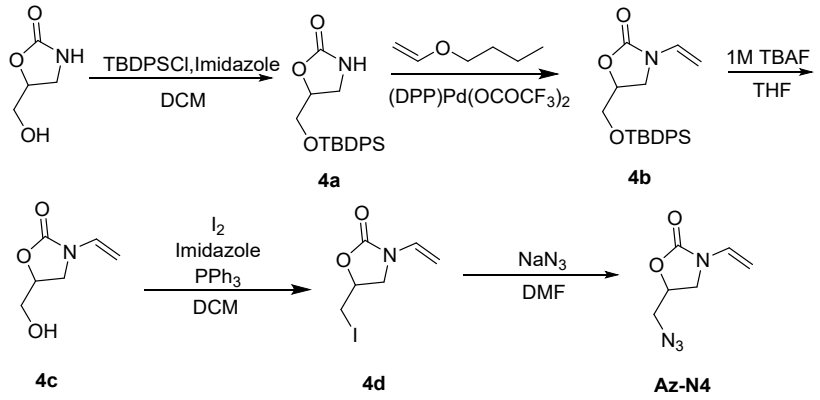
PQ2 NVM PQ2-NVM

PQ2-NVM

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.41 (dd, *J* = 4.2, 1.5 Hz, 2H), 8.27 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.21 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 6.93 (s, 2H), 6.14 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.21 (dd, *J* = 11.0, 9.0 Hz, 1H), 4.65 (dd, *J* = 11.0, 2.6 Hz, 1H), 4.04 (d, *J* = 5.1 Hz, 6H).^{13}C NMR (126 MHz, Chloroform-d) δ 168.9, 167.2, 135.1, 128.9, 128.8, 127.4, 127.3, 126.7, 125.1, 125.1, 121.4, 121.2, 73.9, 64.0, 52.4. m/z: $[M+H]^+$ calcd:448.1032; found:448.1032.

4. Design, synthesize and characterize of double-handled molecule Az-N4

5-(azidomethyl)-3-vinyloxazolidin-2-one (Az-N4)



5(((tert-butyldiphenylsilyl)oxy)methyl)oxazolidin-2-one (4a)

5-(hydroxymethyl)oxazolidin-2-one (2.34g, 20mmol, 1.0eq) and imidazole (5.4g, 80mmol, 4.0eq) were adder to a round bottomed flask. Followed by 100ml DCM, TBDPSCl (13ml, 50mmol, 2.5eq) were added and stirred at room temperature overnight. Reaction completion was confirmed by TLC. The reaction mixture was diluted with dichloromethane, the phases were separated and the organic layer was washed with water and dried over anhydrous Na_2SO_4. Upon removal of solvents in vacuo, the residual was purified by silica gel column chromatography to obtain **4a** (white solid, 6.4g，90% yeild). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.56 (m, 5H), 7.53 – 7.32 (m, 5H), 6.43 (s, 1H), 4.75 – 4.62 (m, 1H), 3.86 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.76 (dd, *J* = 11.3, 3.9 Hz, 1H), 3.67 – 3.54 (m, 2H), 1.07 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 135.5, 135.5, 132.9, 132.6, 129.9, 127.8, 76.2, 64.2, 42.2, 26.6, 19.2. m/z: $[M+Na]^+$ calcd:378.1496; found:378.1488.

5(((tert-butyldiphenylsilyl)oxy)methyl)-3-vinyloxazolidin-2-one (4b)[5]

4a (3.55g, 10 mmol, 1.0eq), BVE (13ml, 100 mmol, 10.0eq), and $(DPP)Pd(OCOCF_3)_2$ (0.34g, 0.5 mmol, 0.05eq) were added in a round bottom flask. The flask was capped by a rubber septum with an 18 gauge needle punctured through it. The reaction was stirred at 75 °C in an oil bath and monitored for completion by TLC. Upon completion, the reaction mixture was allowed to cool and loaded directly onto a silica gel column chromatography to obtain **4b** (pale yellow liquid, 3.87g, 99% yeild). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 5H), 7.48 – 7.43 (m, 5H), 6.94 (dd, *J* = 15.8, 8.9 Hz, 1H), 4.73 – 4.66 (m, 1H), 4.45 (dd, *J* = 9.0, 1.2 Hz, 1H), 4.31 (dd, *J* = 15.8, 1.2 Hz, 1H), 3.95 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.79 – 3.67 (m, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 135.7, 135.6, 132.9, 132.4, 130.0, 130.0, 129.9, 127.9, 127.9, 93.1, 73.7, 64.3, 43.6, 26.7, 19.2. m/z: $[M+H]^+$ calcd:382.1833; found:382.1826.

5-(hydroxymethyl)-3-vinyloxazolidin-2-one (4c)

4b (1.9 g, 5 mmol, 1.0eq) was dissolved in 10ml anhydrous THF in a round bottom flask, then 1 M solution of TBAF in THF (7.5 mL, 7.5 mmol, 1.5eq) was added at room temperature. The solution was stirred for 2 h and monitored for completion by TLC. The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatographyl to obtain **4c** (pale yellow liquid, 0.6 g, 84% yeild). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.74 (dd, J = 15.8, 8.9 Hz, 1H), 5.17 (t, J = 5.6 Hz, 1H), 4.73 – 4.65 (m, 1H), 4.40 – 4.31 (m, 2H), 3.69 (t, J = 9.2 Hz, 1H), 3.64 (ddd, J = 12.3, 5.3, 3.3 Hz, 1H), 3.50 (ddd, J = 12.3, 5.7, 3.9 Hz, 1H), 3.45 (dd, J = 9.2, 6.2 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ 155.1, 130.2, 93.8, 74.9, 62.0, 43.5. m/z: $[M+Na]^+$ calcd:144.0655; found:144.0653.

5-(iodomethyl)-3-vinyloxazolidin-2-one (4d)

I_2 (1.22g, 4.8mmol, 1.2eq), PPh_3(1.26g, 4.8mmol, 1.2eq) and imidazole (0.41g, 6.0mmol, 1.5eq) were dissolved in 30ml anhydrous DCM in a round bottom flask and the mixture was stirred at room temperature for 5 min. A solution of compound **4c** (0.57g, 4mmol, 1.0eq) in 10ml anhydrous DCM was added dropwise to the mixture. The reaction was stirred at room temperature 2.5 hours and monitored for completion by TLC. The solvent was evaporated in vacuo, and the residue was purified by silica gel column chromatographyl to obtain **4d** (colorless liquid, 0.86 g, 85% yeild). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.79 (ddd, J = 15.6, 9.0, 4.1 Hz, 1H), 4.72 – 4.62 (m, 1H), 4.42 (ddd, J = 9.0, 3.0, 1.4 Hz, 1H), 4.30 (dt, J = 15.8, 1.7 Hz, 1H), 3.81 (td, J = 9.0, 2.0 Hz, 1H), 3.42 – 3.37 (m, 2H), 3.30 (dd, J = 10.4, 7.7 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-d) δ 154.2, 129.4, 94.1, 72.3, 48.0, 6.7. m/z: $[M+H]^+$ calcd:253.9678; found:253.9670.

5-(azidomethyl)-3-vinyloxazolidin-2-one (Az-N4)

4d (0.73g, 2.88mmol, 1.0eq) and sodium azide (0.56g, 8.66mmol, 3.0eq) was added into 5 mL of DMF in a round bottom flask and the resulting mixture was heated to 65 ºC for 2 h. Reaction completion was confirmed by TLC. The reaction mixture was diluted with ethyl acetate, washed with H_2O (3×30 mL) and brine (20 mL) and dried over Na_2SO_4. Upon removal of solvents in vacuo, the residual was purified by silica gel column chromatography to obtain **N4-N$_3$** (colorless liquid, 0.40 g, 82% yeild). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.82 (dd, J = 15.8, 9.0 Hz, 1H), 4.80 – 4.71 (m, 1H), 4.43 (dd, J = 9.0, 1.4 Hz, 1H), 4.28 (dd, J = 15.8, 1.4 Hz, 1H), 3.74 (t, J = 9.2 Hz, 1H), 3.64 (dd, J = 13.3, 4.2 Hz, 1H), 3.55 – 3.44 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 154.1, 129.4, 93.9, 71.8, 53.0, 44.2. m/z: [M+H]+ calcd:169.0718; found:169.0720.

5. Kinetics Studies

The reaction rate constants of cycloaddition between PQ derivatives and N-vinyl compounds were calculated based on HPLC analysis results. All compound storage solvent is MeCN. All kinetics experiments were carried out at room temperature in MeCN/PBS=1/1. Second-order kinetics was performed by combining PQ derivatives and N-vinyl compounds in a 1:10 ratio, and the concentration of PQ derivatives is 125 μM. The relative amounts of PQ derivatives and the product were monitored by absorbance at 254 nm and calculated by integration of areas at 254 nm. Percent conversion (x) was calculated by both disappearance of PQ derivatives and appearance of the product. Pseudo-first order rate constant *k*obs was determined by plotting ln[1/(1-x)] versus time and analysis by linear regression (x represents the percent conversion of PQ derivatives). The slope of the linear equation is *k*obs. The second rate constant *k*2 was calculated by *k*obs/[N-vinyl compounds]. The experimental results are presented in Fig. S2.

6. Fluorescence measurement

The fluorescence spectrum of the reaction between PQ, PQ1, or PQ5 and N4 (Fig. 3B)

A solution containing **PQ**, **PQ1,** or **PQ5** (125μM) and **N4** (1.25 mM) in CH_3CN/PBS (1/1) was irradiated for 30 seconds using a hand-held white-light LED lamp. The fluorescence spectrum was subsequently recorded. Ex, 365 nm.

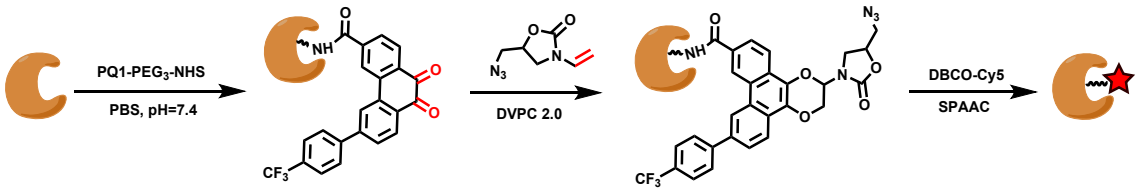
The fluorescence spectrum of the reaction between PQ2 and NVM (Fig. 3C)

(a) A mixture of **PQ2** (125μM) and **NVM** (1.25 mM) was prepared in CH_3CN/PBS (1/1) and analyzed by fluorescence spectroscopy. Ex, 365 nm. (b) A mixture of **PQ2** (125μM) and **NVM** (1.25 mM) was irradiated with white light (200mW/cm^2, 10 min) and analyzed by fluorescence spectroscopy. Ex, 365 nm. (c) Following the same irradiation conditions as in (b) , **Cys** (1.25 mM) was added to the reaction mixture, and fluorescence analysis was performed. Ex, 365 nm.

The fluorescence spectrum of the reaction between PQ2 and N4 by two-photon excitation (Fig. 3D)

The mixture of **PQ2** (100μM) and **N4** (1mM) in CH_3CN/PBS (1/1) was irradiated via two-photon excitation using a Mai Tai HP ultrafast tunable laser. The laser was operated at 30% output power with sequential excitation wavelengths of 700, 720, 740, 760, 780, and 800 nm. Following irradiation, the fluorescence properties of the samples were characterized. Ex, 365 nm.

7. Protein labeling



Preparation of the modified protein PQ1-PEG$_3$-BSA

A solution of BSA (2 mg/mL) in PBS (pH = 7.4) was mixed with 100 equivalents of **PQ1-PEG$_3$-NHS ester** and was shaken (900rpm) at room temperature for 4 h. Unconjugated **PQ1-PEG$_3$-NHS ester** was removed by repeated rounds of centrifugation using a 30 kDa filter to give purified **PQ1-PEG$_3$-BSA** solution. The concentration of **BSA-PEG$_3$-PQ1** was quantified with BCA protein assay kit (Pierce).

In-gel fluorescence assay

(1) Time-dependent reaction between BSA-PEG$_3$-PQ1 and Az-N4

For time-dependent reaction, **PQ1-PEG$_3$-BSA** (2mg/mL) and 300.0eq **Az-N4** were irradiated in PBS at room temperature with 200mW/cm^2 at 420nm for 0-180s, then 300.0eq **DBCO-Cy5** was add and let it stand for 1 hour. Protein samples (20 μg) were further analyzed by gel electrophoresis using 8% polyacrylamide gels and imaged with Bio-Rad Chemdoc imaging system using corresponding filters. Protein loading was assessed by staining with Coomassie Blue according to manufacturer's instructions.

(2) Light intensity dependent reaction between BSA-PEG$_3$-PQ1 and Az-N4

For light intensity-dependent reaction, **PQ1-PEG$_3$-BSA** (2mg/mL) and 300.0eq **Az-N4** were irradiated in PBS at room temperature with different optical densities at 420nm for two minutes, then 300.0eq **DBCO-Cy5** was added and let it stand for 1 hour. Protein samples (20 μg) were further analyzed by gel electrophoresis using 8% polyacrylamide gels and imaged with Bio-Rad Chemdoc imaging system using corresponding filters. Protein loading was assessed by staining with Coomassie Blue according to manufacturer's instructions.

Supporting Figures

(a) **(b)**

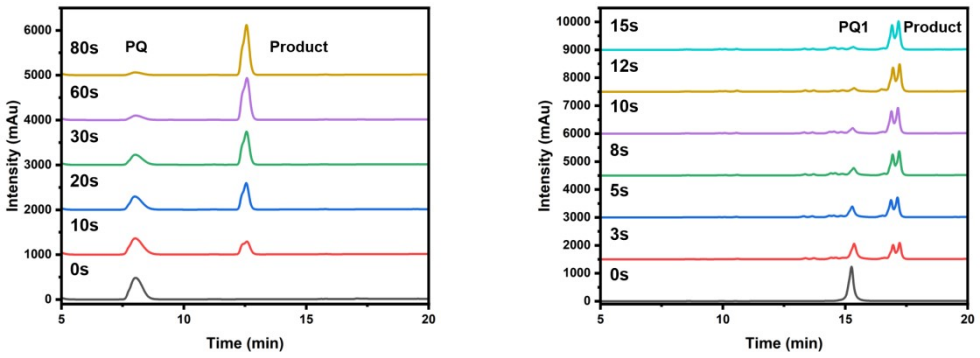


Figure S1. HPLC analysis of (a) the reaction between **PQ** and **NVP**. (b) the reaction between **PQ1** and **N4**. *o*-diones (125 μM) and N-vinyl amides (1.25 mM) were mixed in CH_3CN/PBS (1/1) and exposed to irradiation with the white light for different time points.

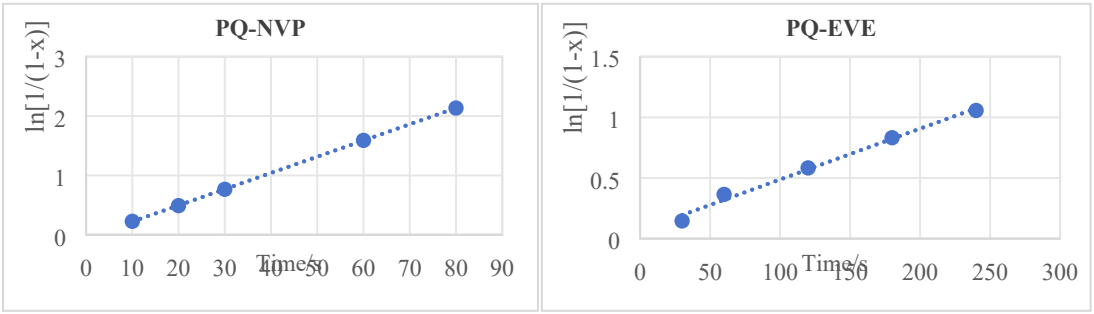
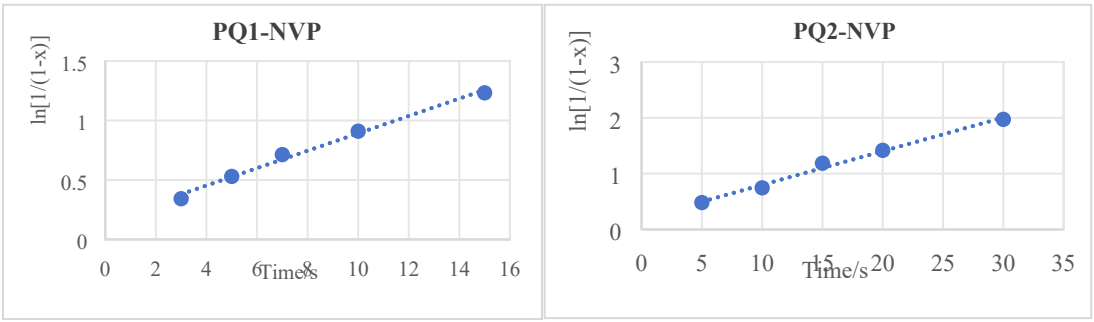


Figure S2. Measurement of second order rate constants of reactions of **PQ** (125 μM) with **NVP/EVE** (1.25 mM) by plotting ln[1/(1-x)] versus time (x represents the percent conversion of *o*-dione). The reaction rate constants were calculated based on HPLC analysis results. Percent conversion (x) was calculated from the integrated area change of *o*-dione at 254 nm. The above reaction occurred in CH_3CN/PBS = 1/1 with 200mW/cm^2 white light irradiation. The reaction conditions and calculation methods for the second order rate constants are the same in S3-S5.



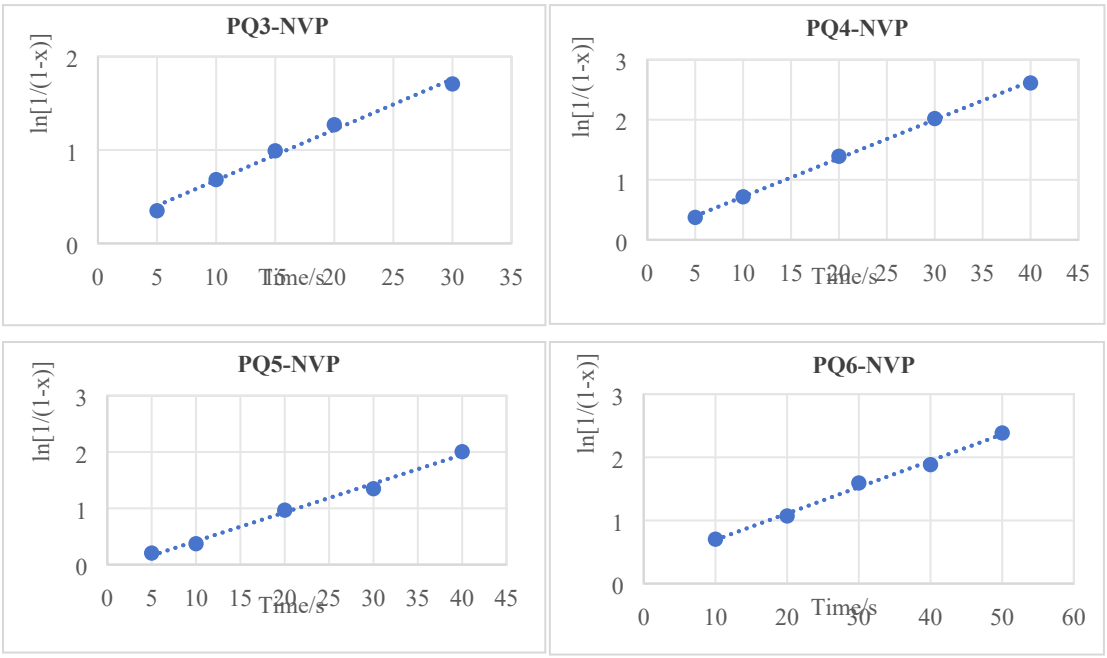


Figure S3. Measurement of second order rate constants of reactions of **PQ1-PQ6** (125 μM) with **NVP** (1.25 mM).

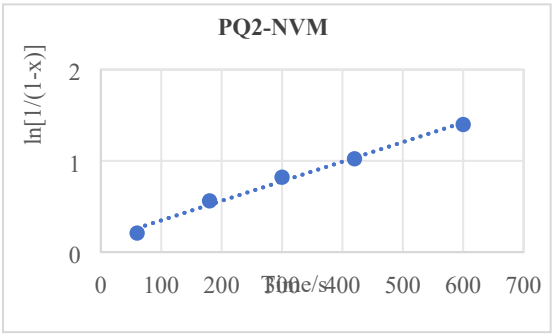


Figure S4. Measurement of second order rate constants of reactions of **PQ2** (125 μM) with **NVM** (1.25 mM).

(a) **(b)**

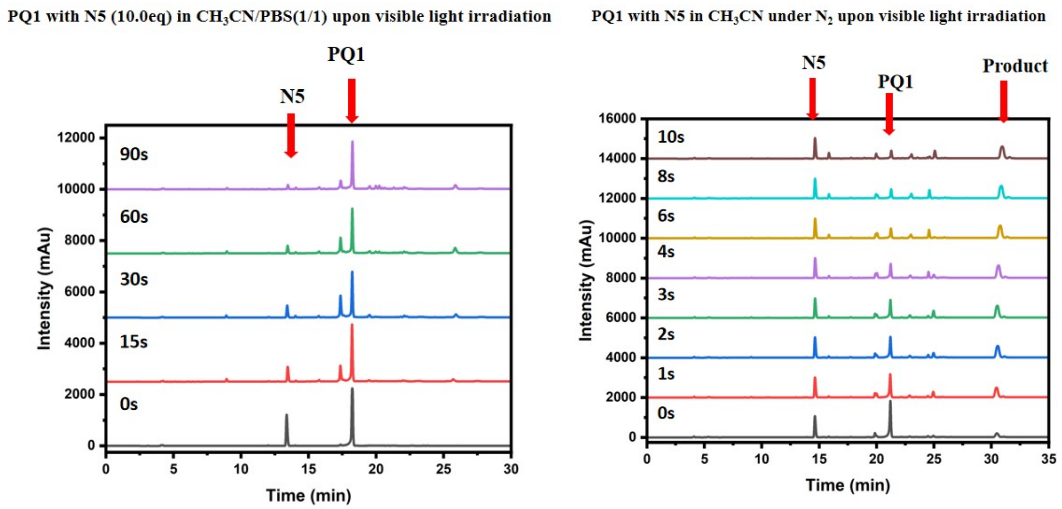
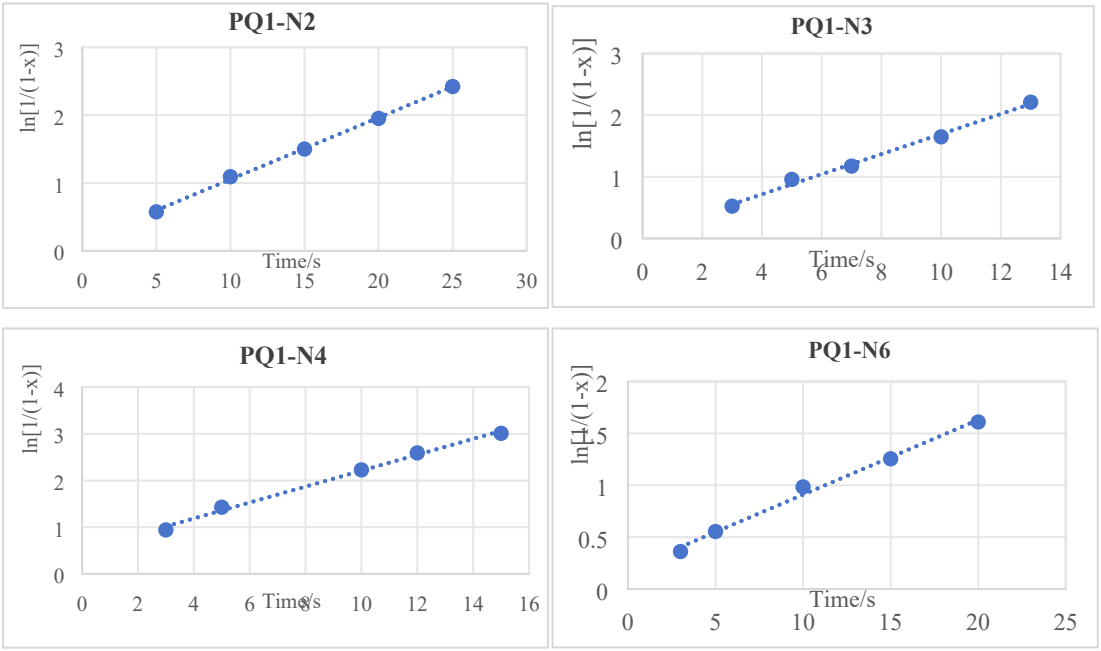


Figure S5. HPLC analysis of (a) the reaction between **PQ1** and **N5** in CH_3CN/PBS (1/1) upon visible light irradiation. (b) the reaction between **PQ1** and **N5** in CH_3CN under N_2 upon visible light irradiation.

(a)



(b)

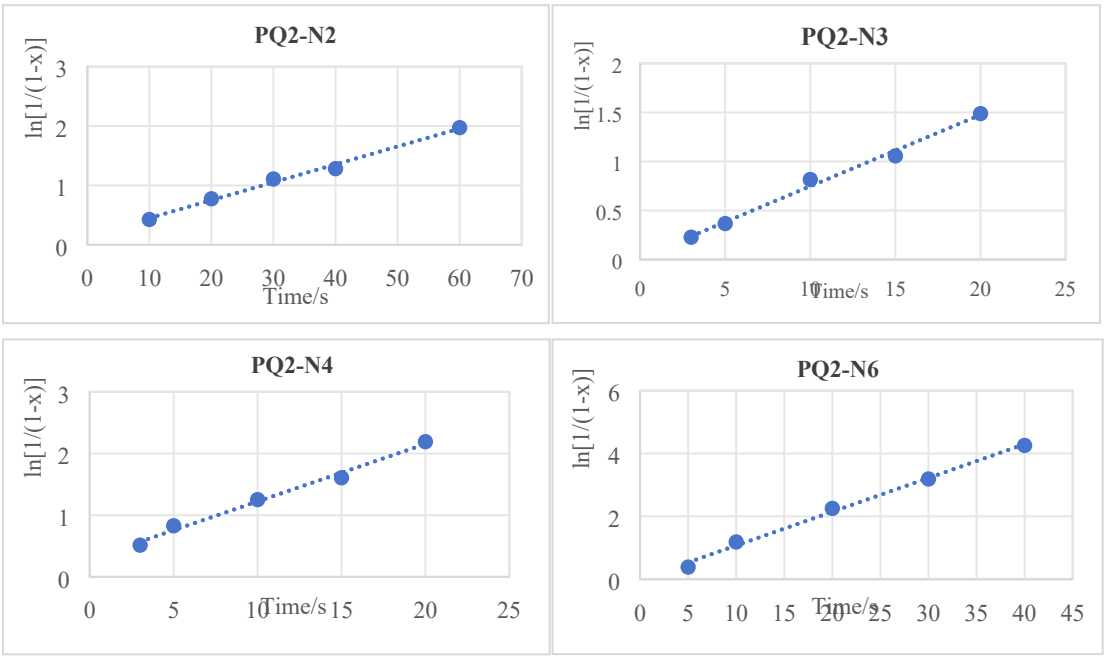
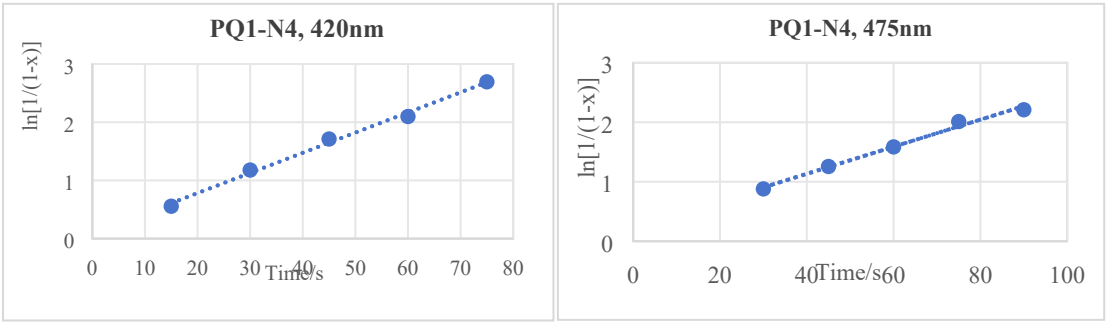


Figure S6. Measurement of second order rate constants of (a) reactions of **PQ1** (125 μM) with **N2-N4, N6** (1.25 mM). (b) reactions of **PQ2** (125 μM) with **N2-N4, N6** (1.25 mM).

(a)



(b)

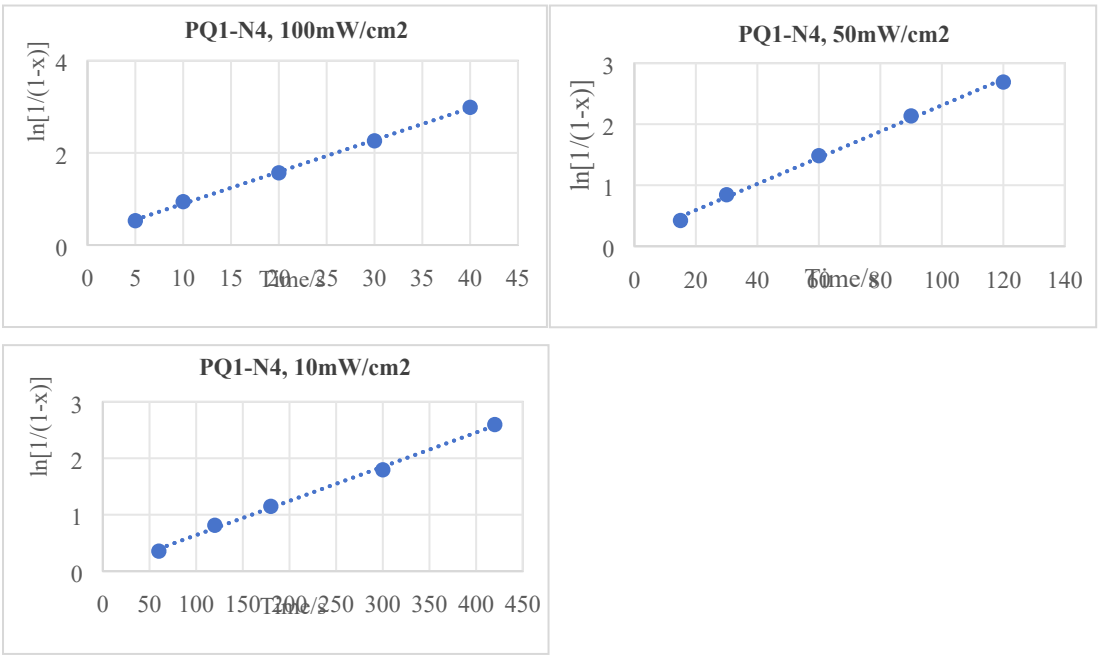


Figure S7. Measurement of second order rate constants of reactions of (a) reactions of **PQ1** (125 μM) with **N4** (1.25 mM) in CH_3CN/PBS = 1/1 with 200mW/cm^2 at 420nm or 475nm irradiation. (b) reactions of **PQ1** (125 μM) with **N4** (1.25 mM) in CH_3CN/PBS = 1/1 with 100mW/cm^2 , 50mW/cm^2 , 10mW/cm^2 white light irradiation by plotting ln[1/(1-x)] versus time (x represents the percent conversion of *o*-dione). The reaction rate constants were calculated based on HPLC analysis results. Percent conversion (x) was calculated from the integrated area change of *o*-dione at 254 nm.

(a) **(b)**

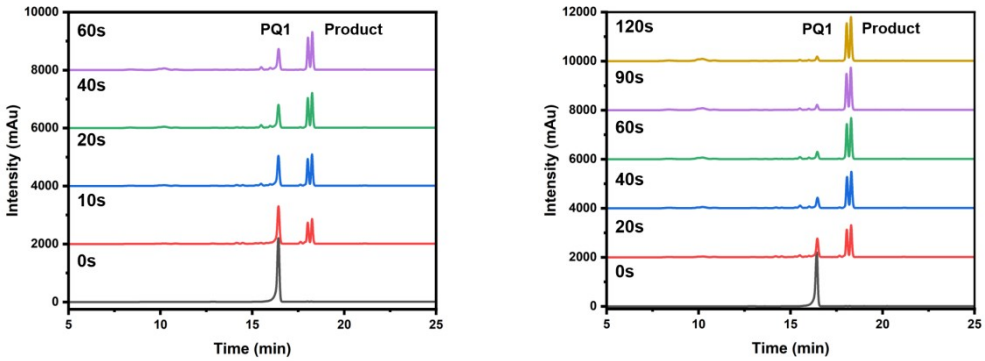


Figure S8. HPLC analysis of (a) **PQ1** (125 μM) / **N4** (250 μM) = 1/2 were mixed in CH_3CN/PBS (1/1) and exposed to irradiation with the white light for different time points. (b) **PQ1**(125 μM) / **N4** (375 μM) = 1/3 were mixed in CH_3CN/PBS (1/1) and exposed to irradiation with the white light for different time points.

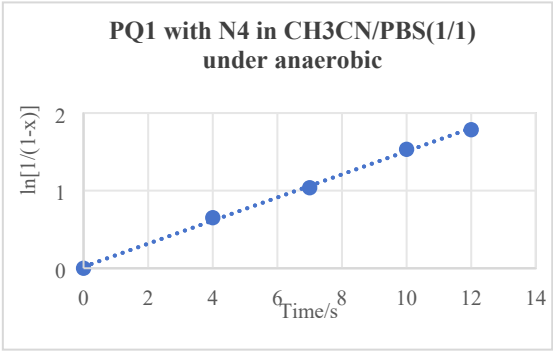


Figure S9 Measurement of second order rate constants of reactions of **PQ1** with **N4** in CH_3CN/PBS(1/1) under anaerobic

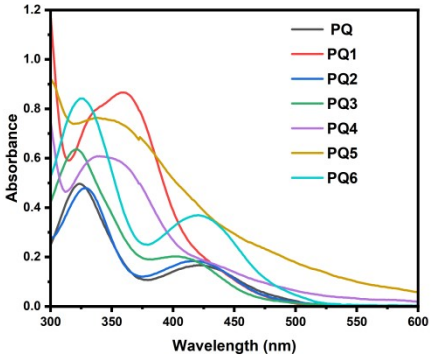
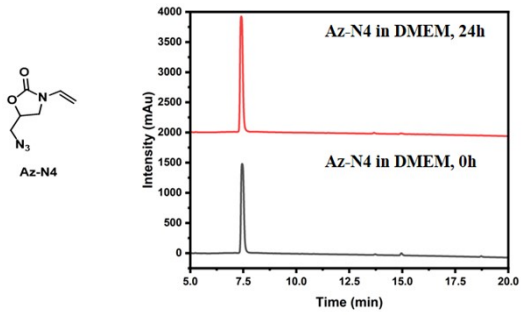


Figure S10. UV-Vis absorption spectra of **PQ** and **PQ1-PQ6** (125μM) were measured in CH_3CN/PBS = 1/1.

(a)



(b)

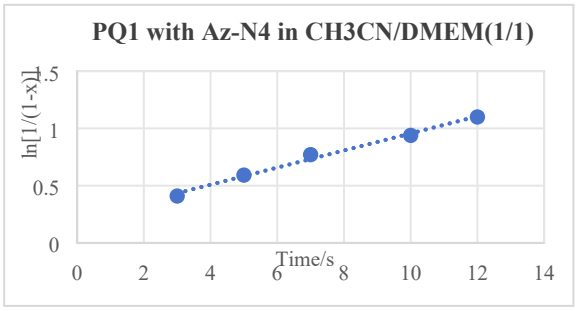


Figure S11. (a) stability of **Az-N4**. (b) reactivity of **Az-N4** under physiological condition.

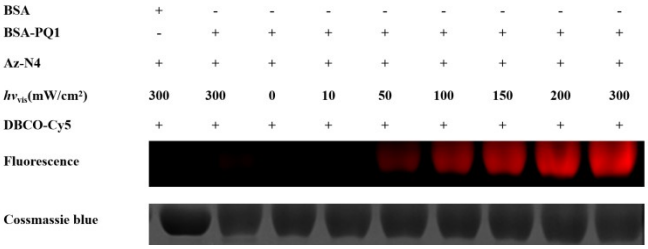


Figure S12. (a) Protein labelling with temporal resolution by sequential DVPC2.0/SPAAC using BSA protein modified with PQ1(**BSA-PQ1**) to reaction with **Az-N4** with temporal control through adjustment of optical density (0-300mW/cm^2), reactant ratio (**BSA-PQ1/Az-N4**) followed by SPAAC-based Cy5 labelling. Coomassie staining was used to assess BSA loading.

Supporting Tables

Table S1. Rate constants of the **PQ2-N4** photo cycloaddition initiated by different optical densities and wavelength range.

Wavelength range	OD (mW/cm^2)	CH_3CN/PBS	k_2 ($M^{-1}s^{-1}$)
White light	100	1/1	55.4
	50		17.2
	10		4.9
420nm light	200		27.7
475nm light	200		18.2

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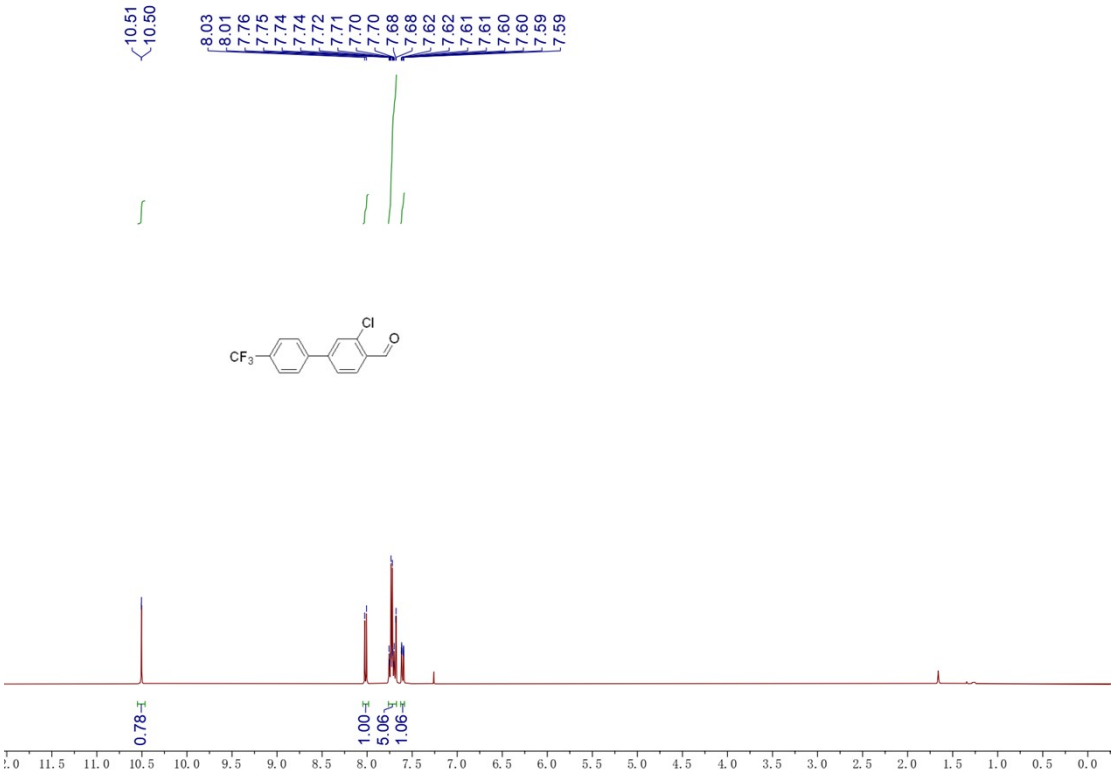
NMR spectra

^{1}H NMR of 1a



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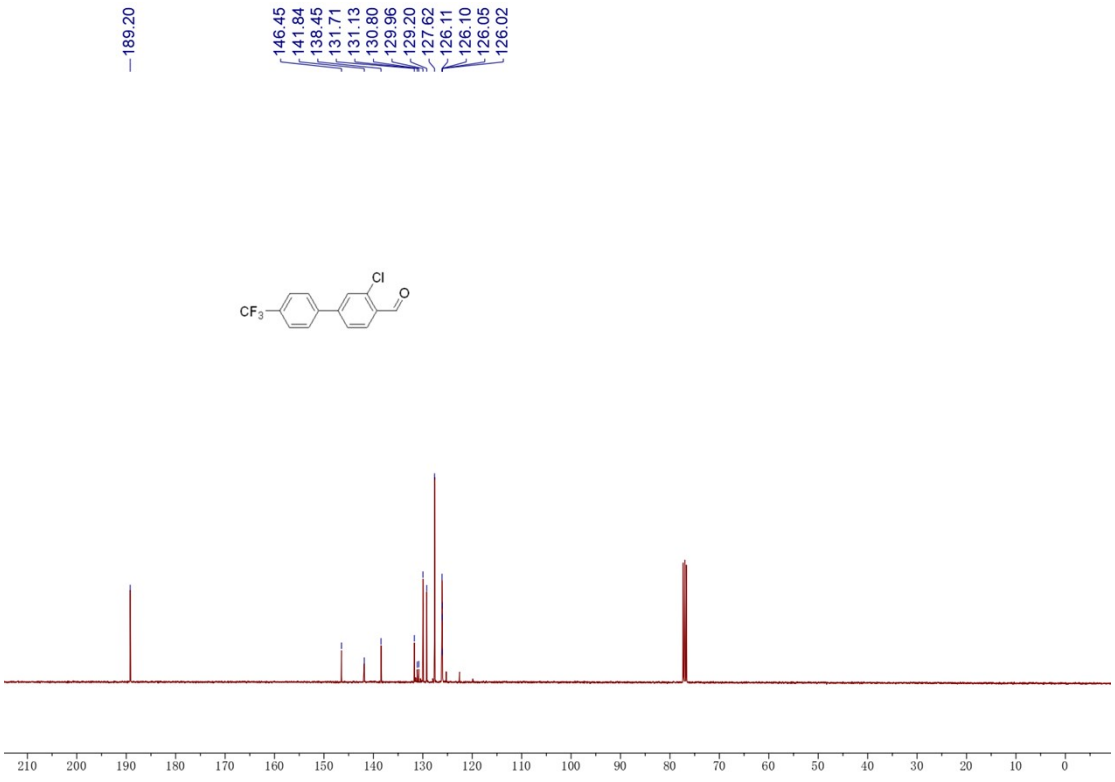

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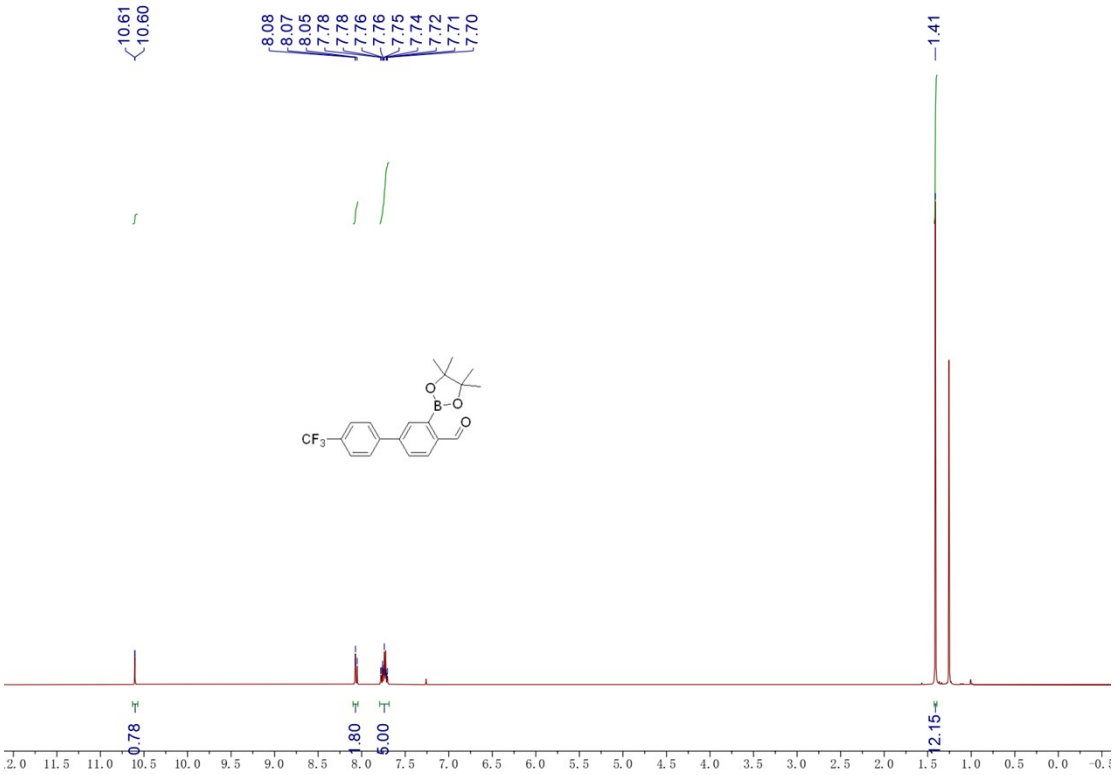

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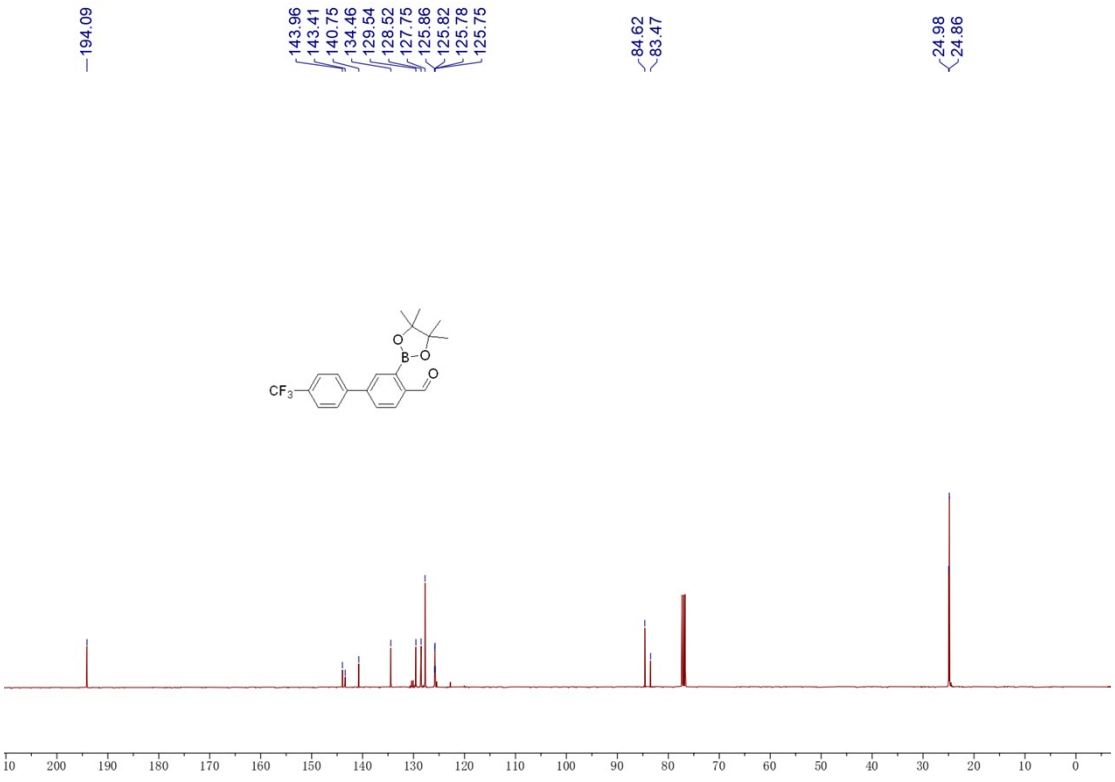

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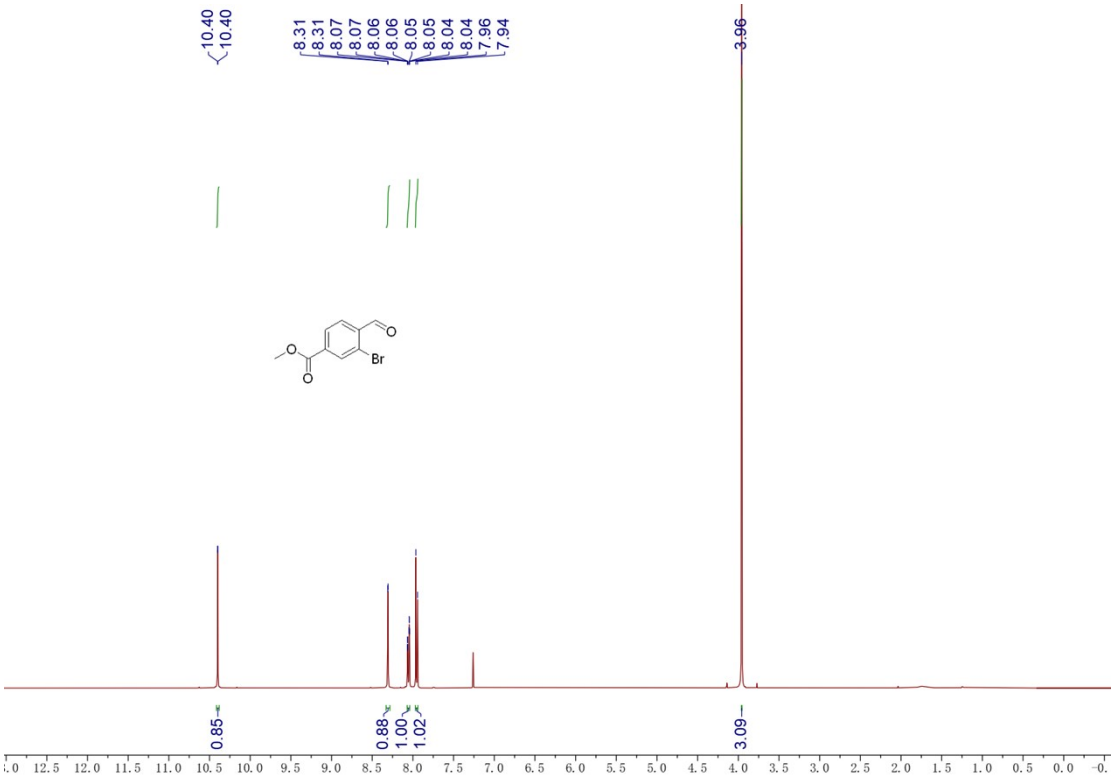

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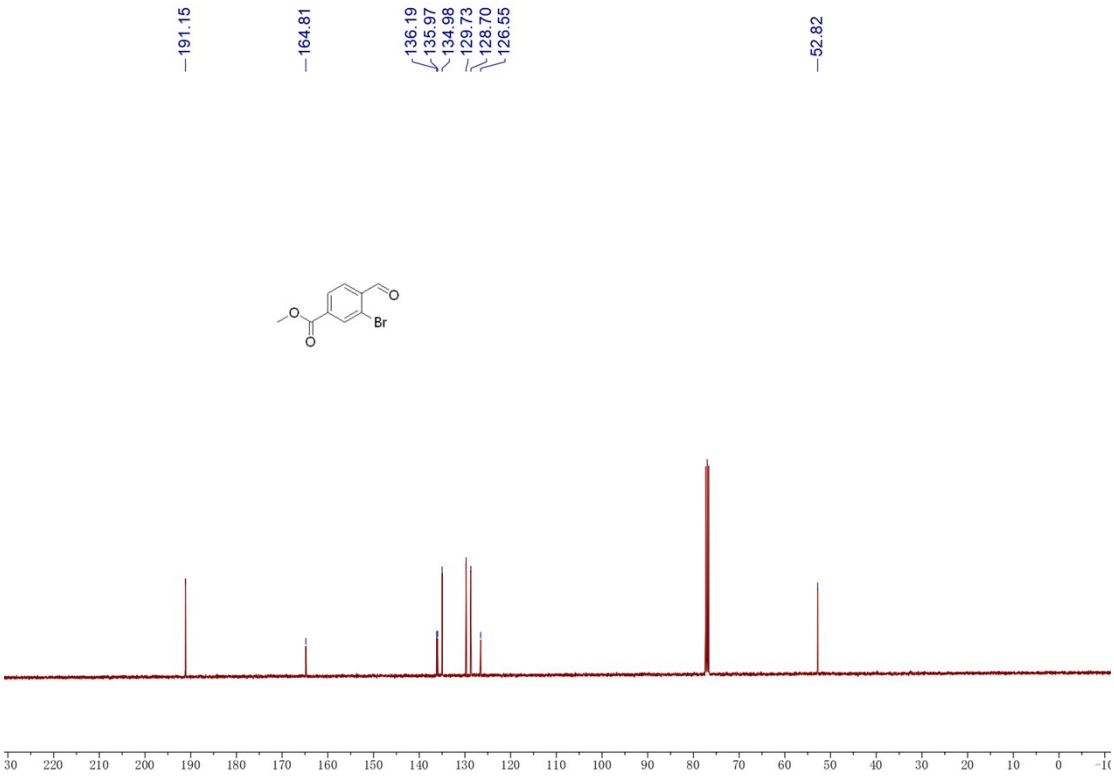

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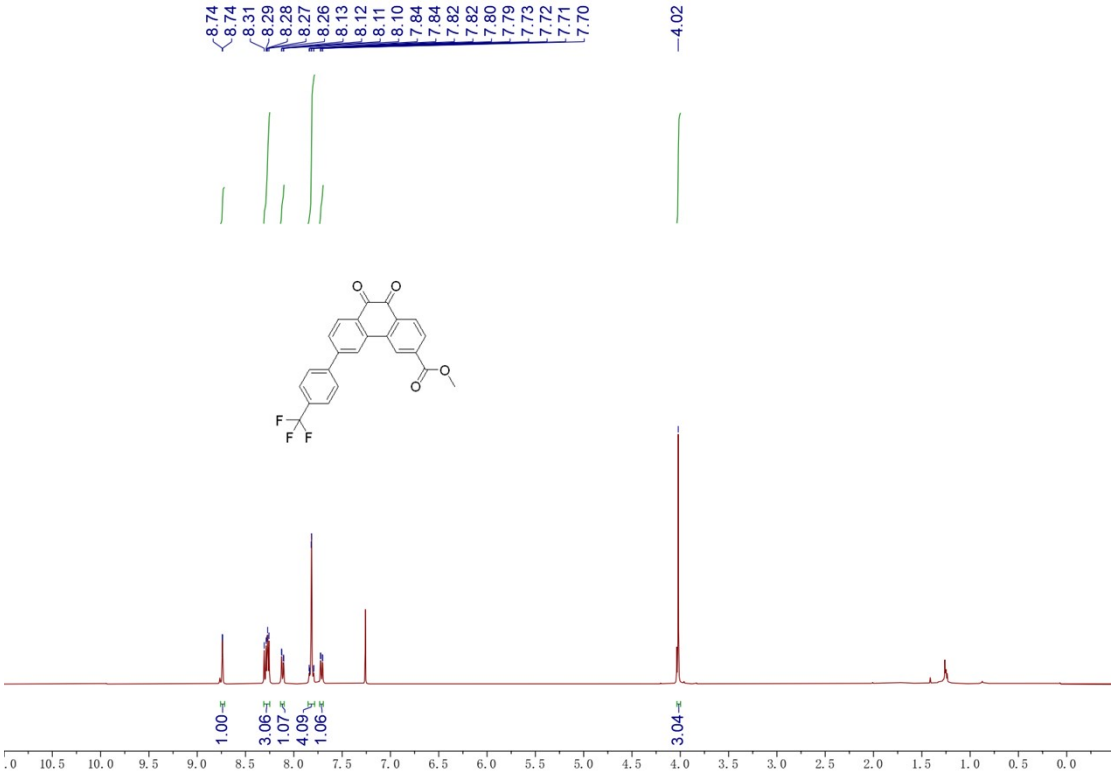

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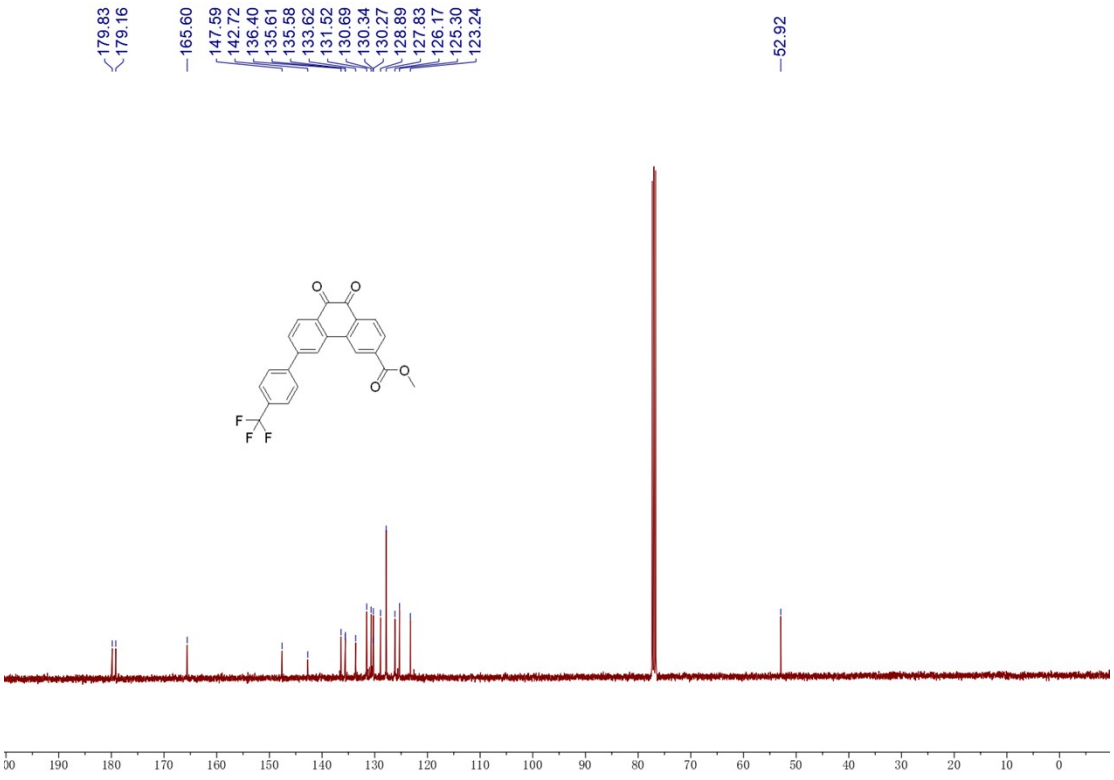

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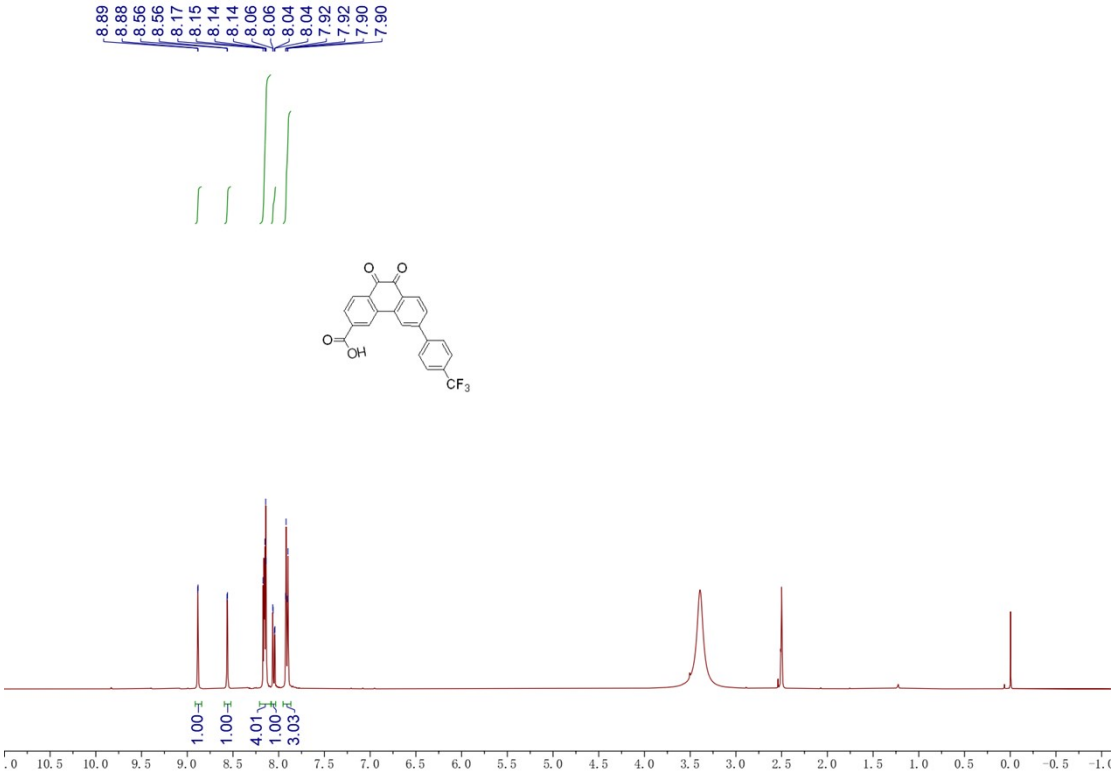

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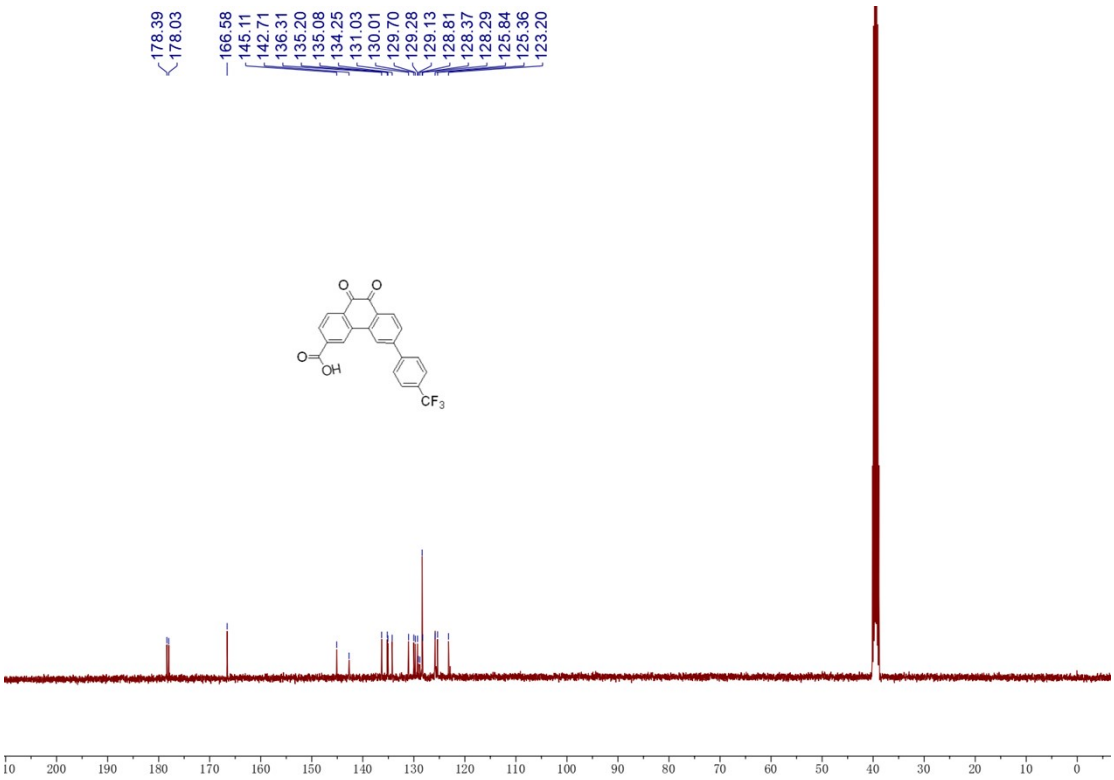

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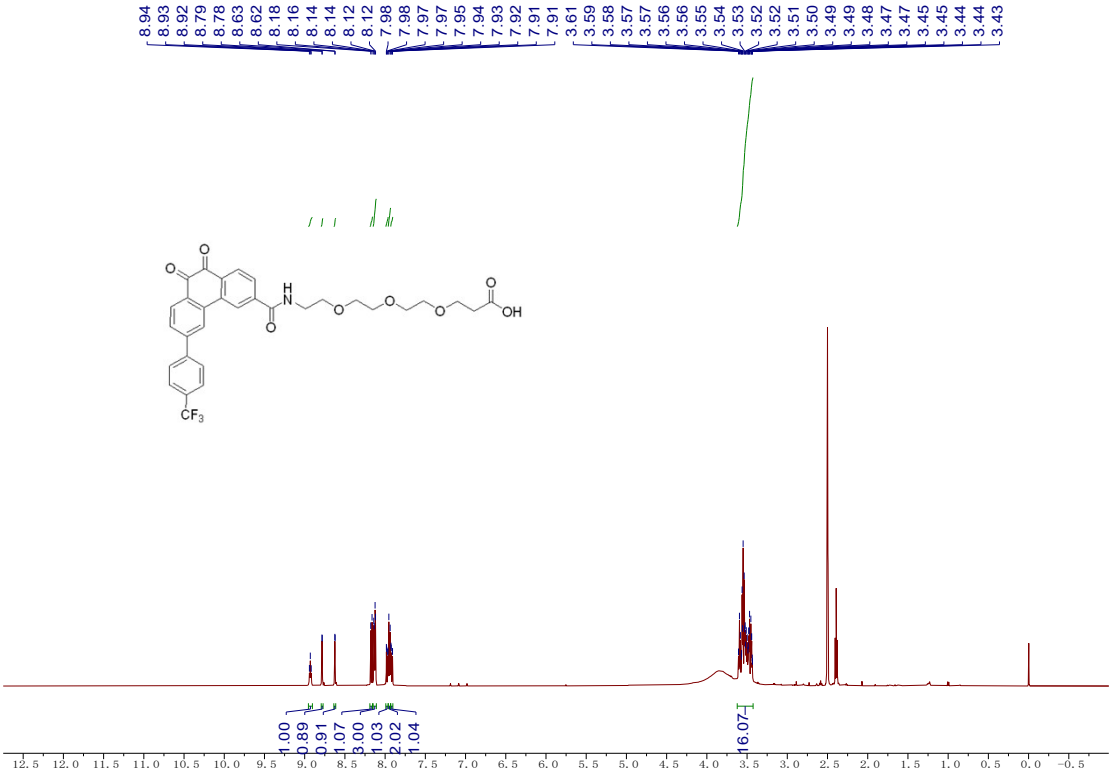

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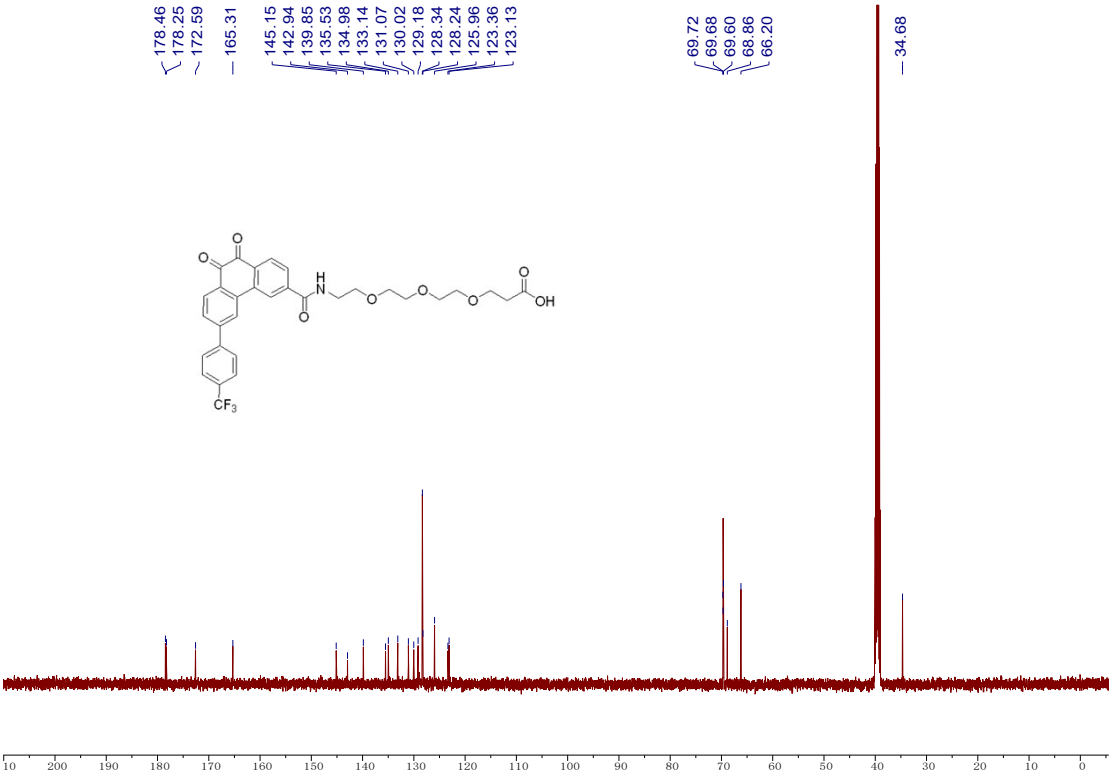

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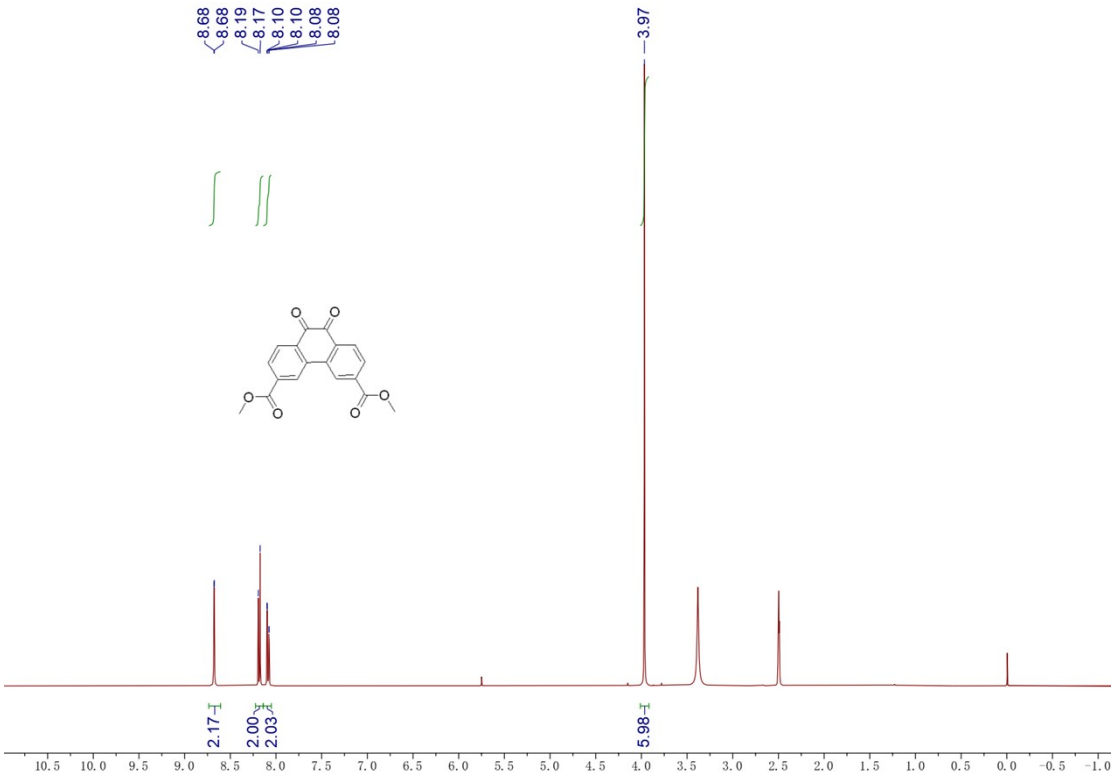

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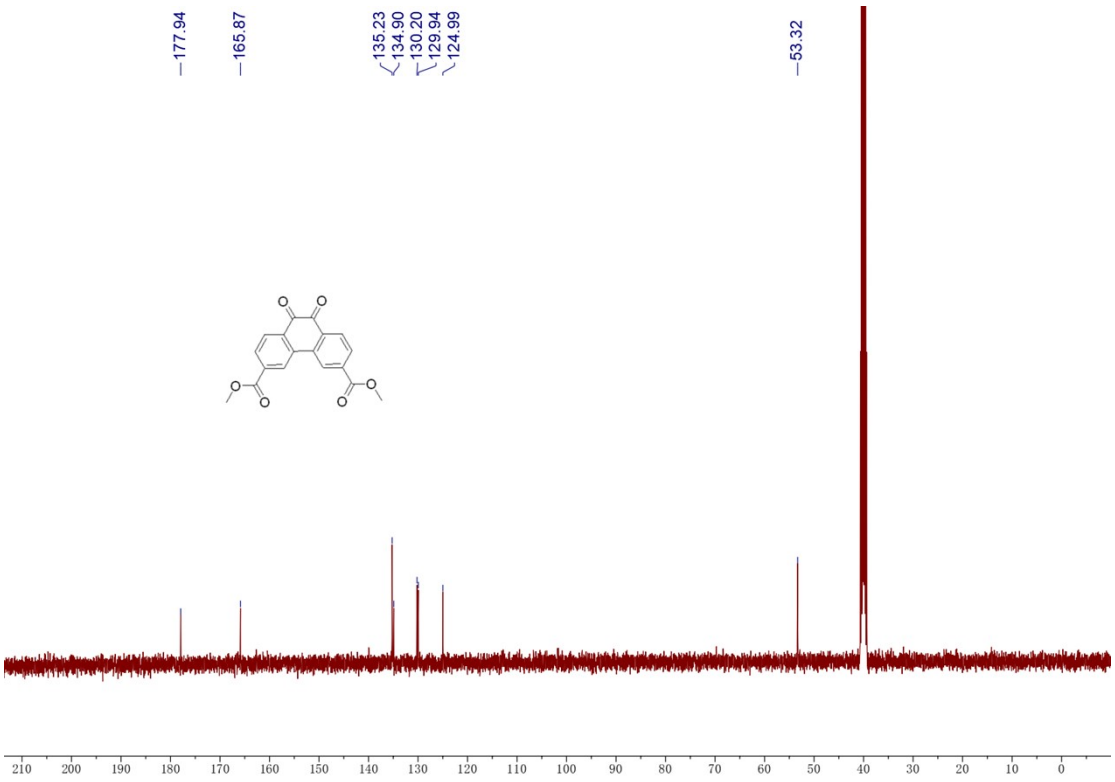

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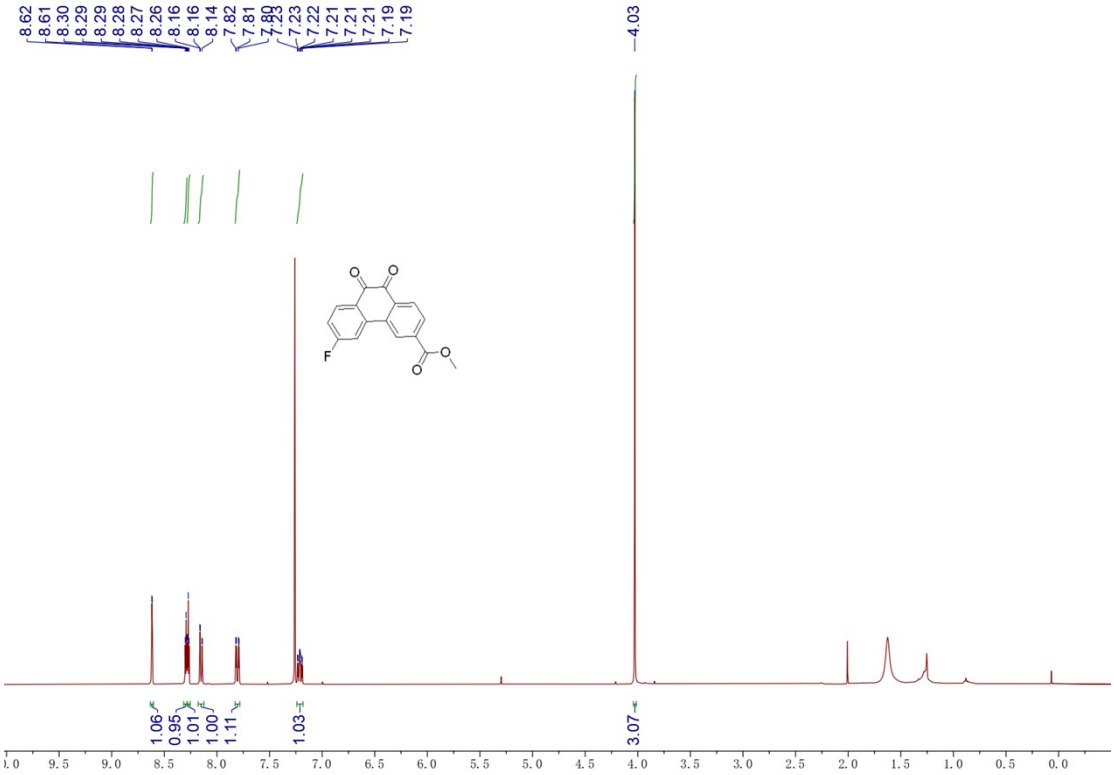

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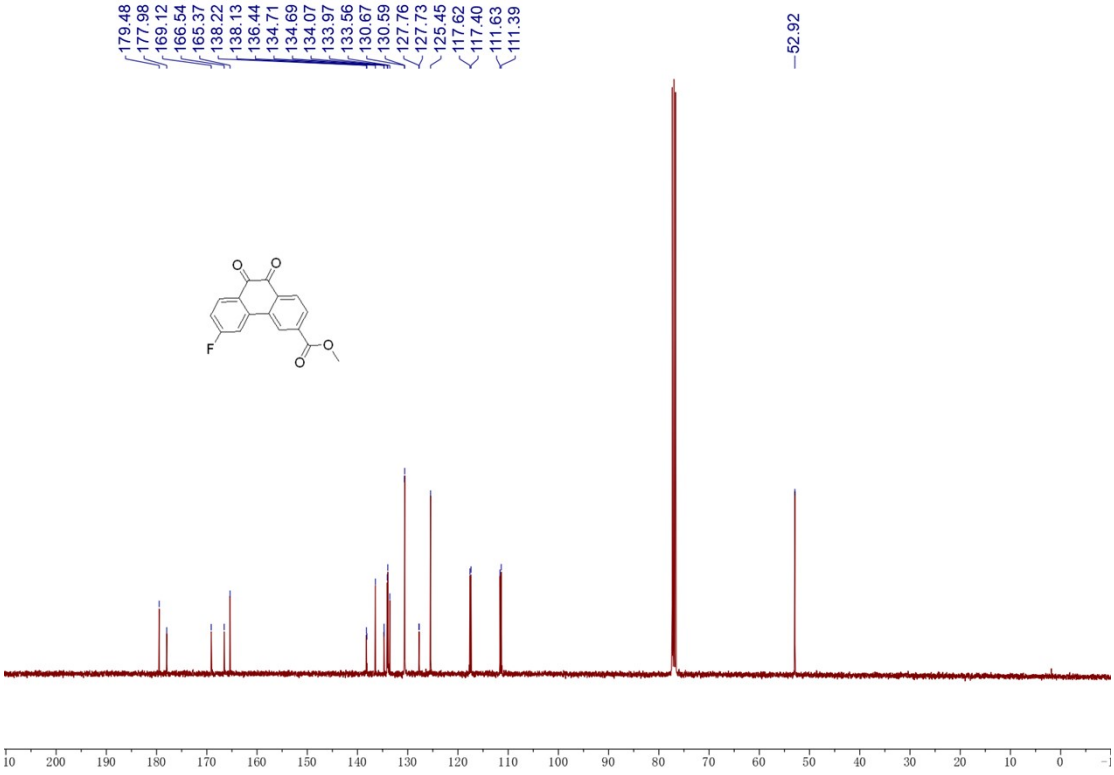

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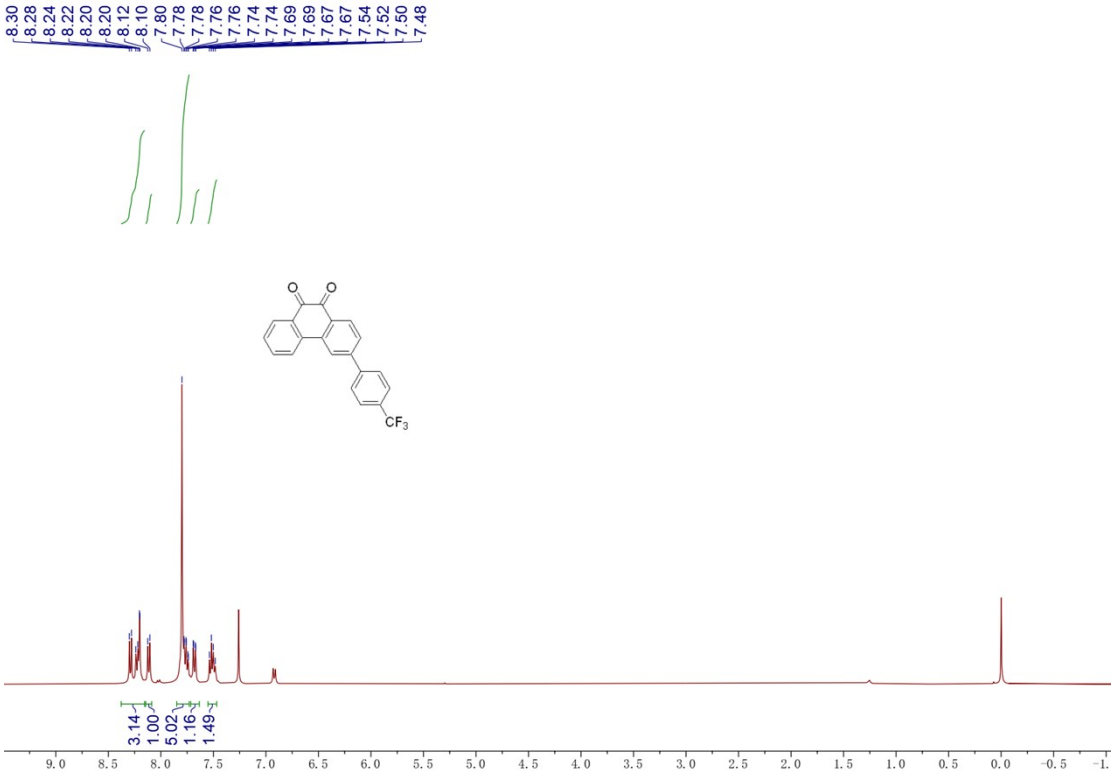

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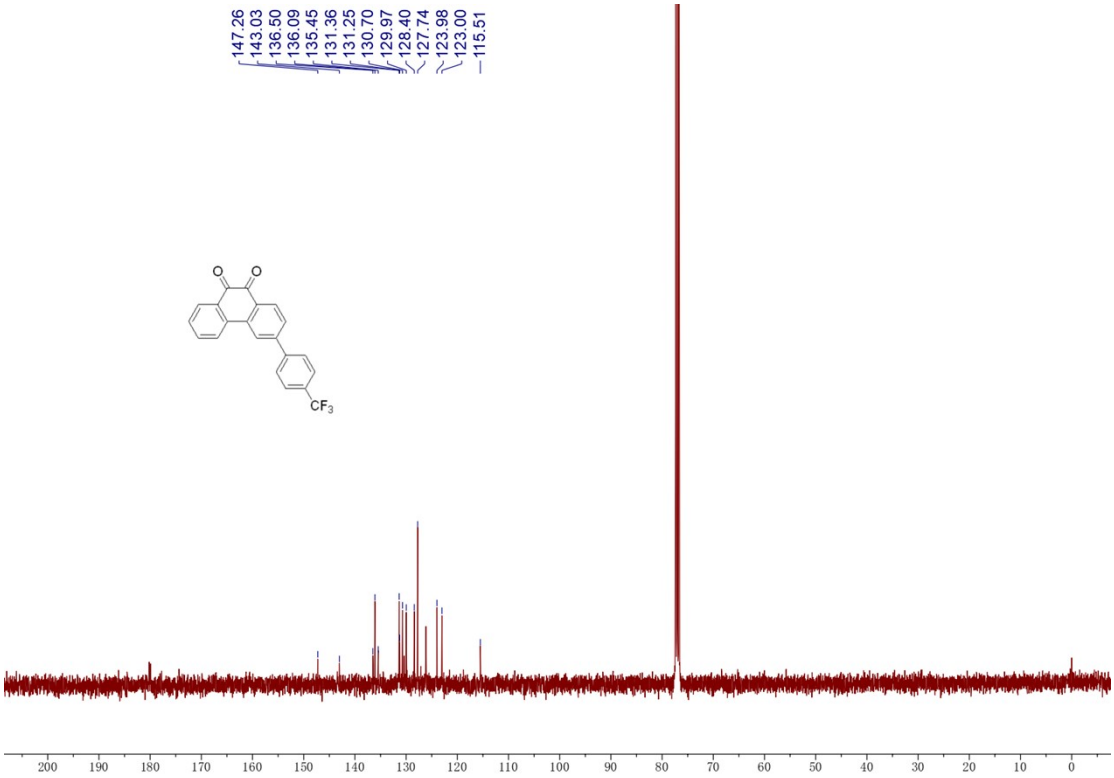

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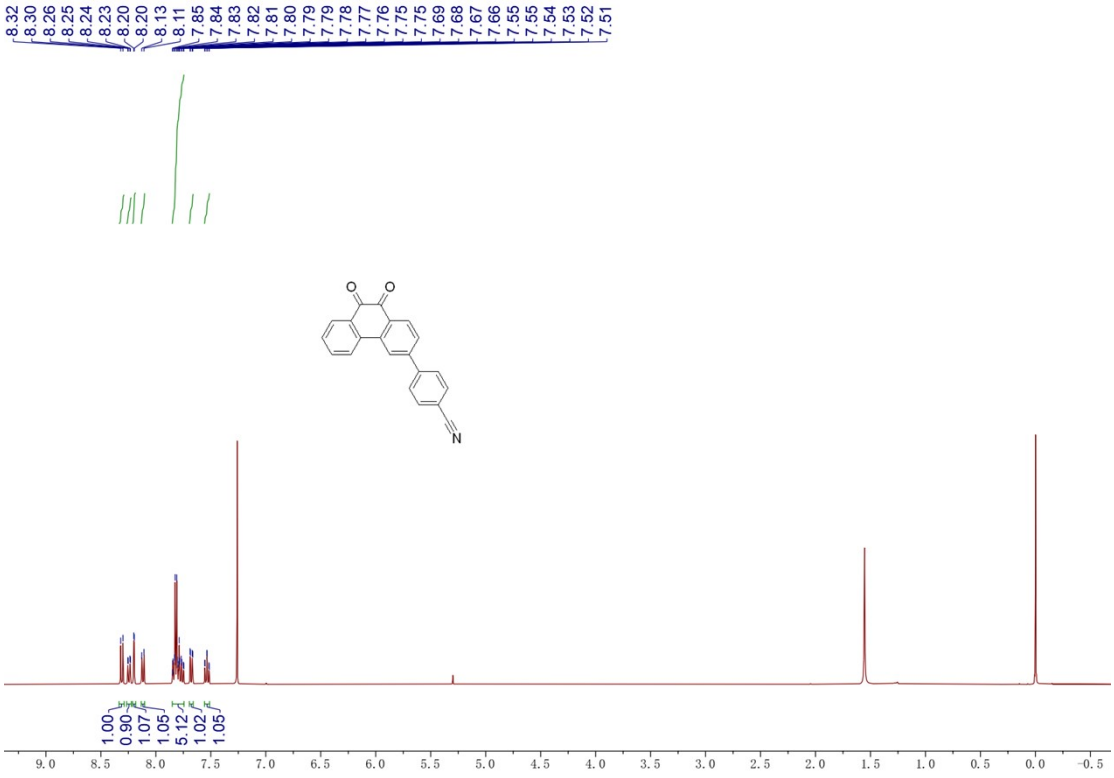

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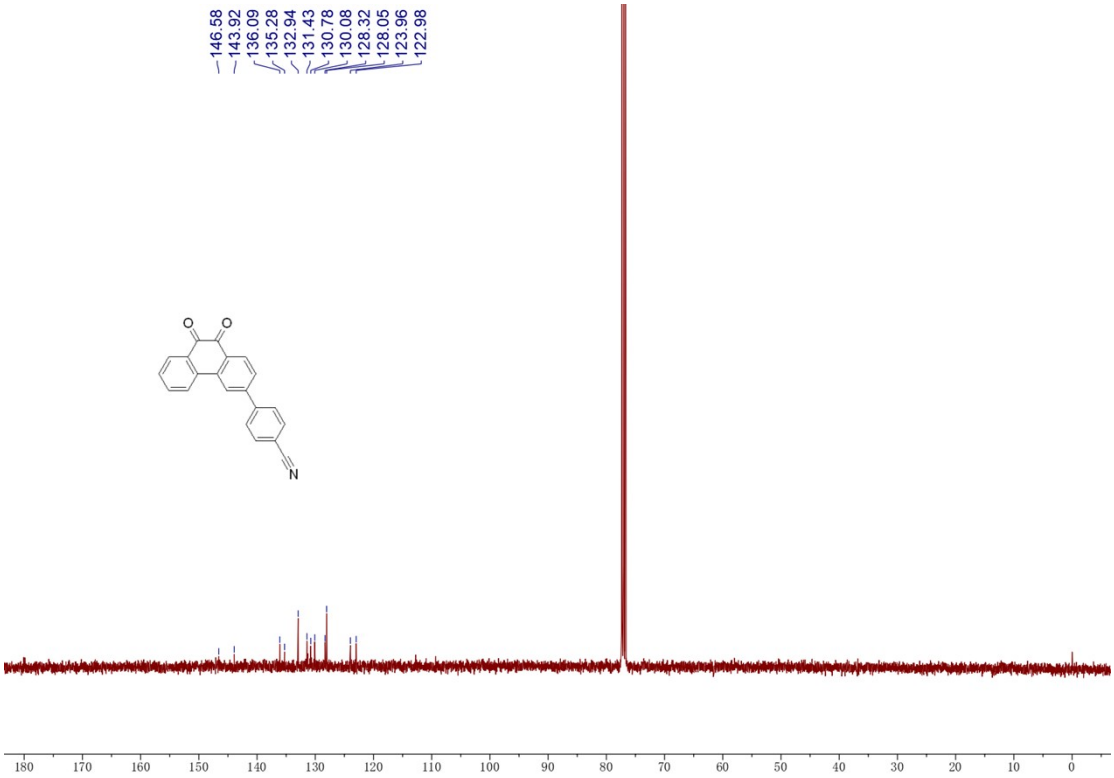

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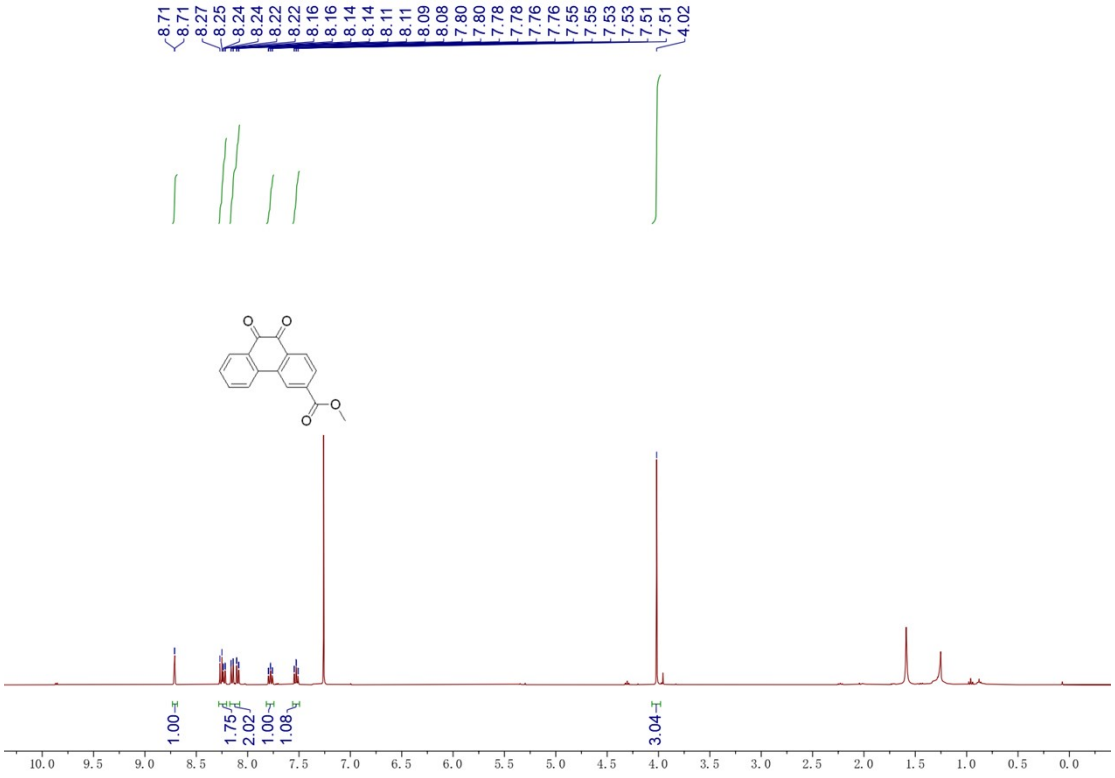

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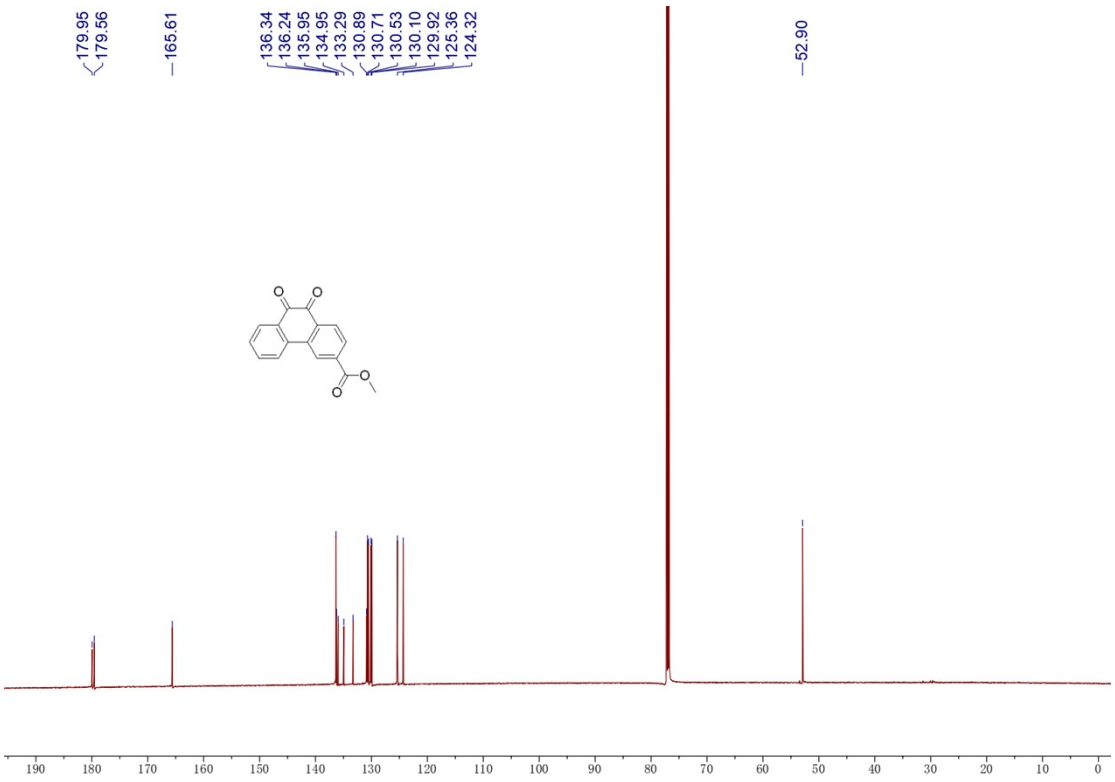

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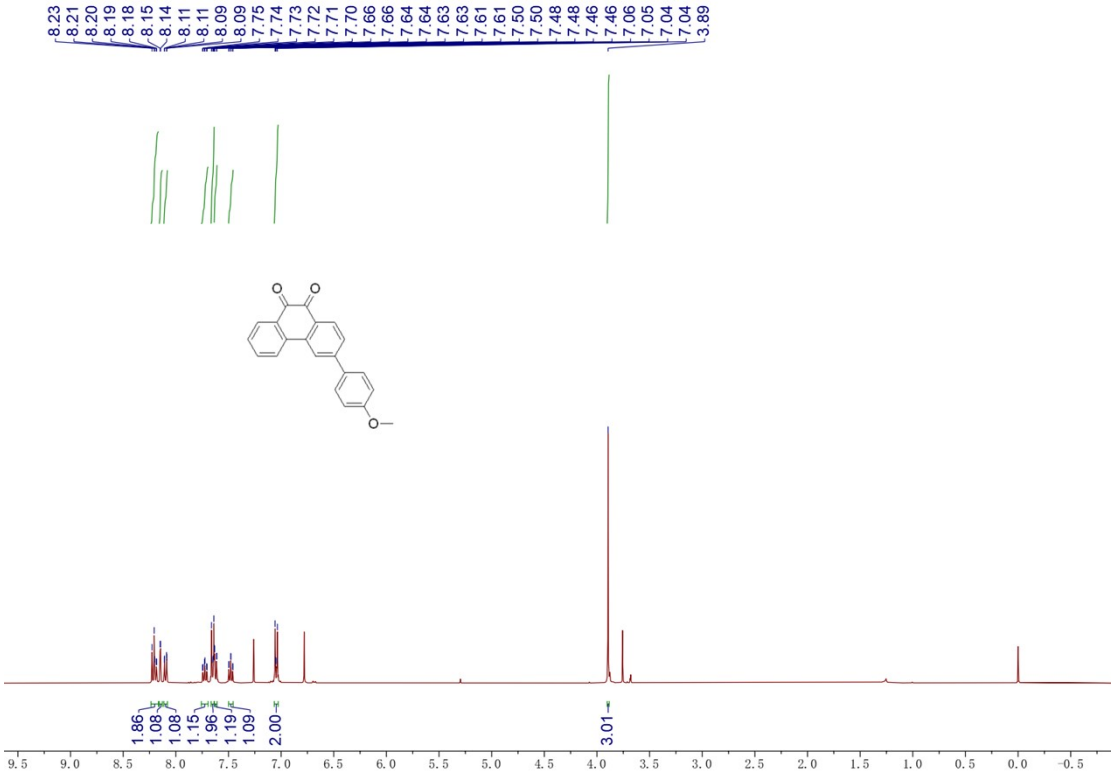

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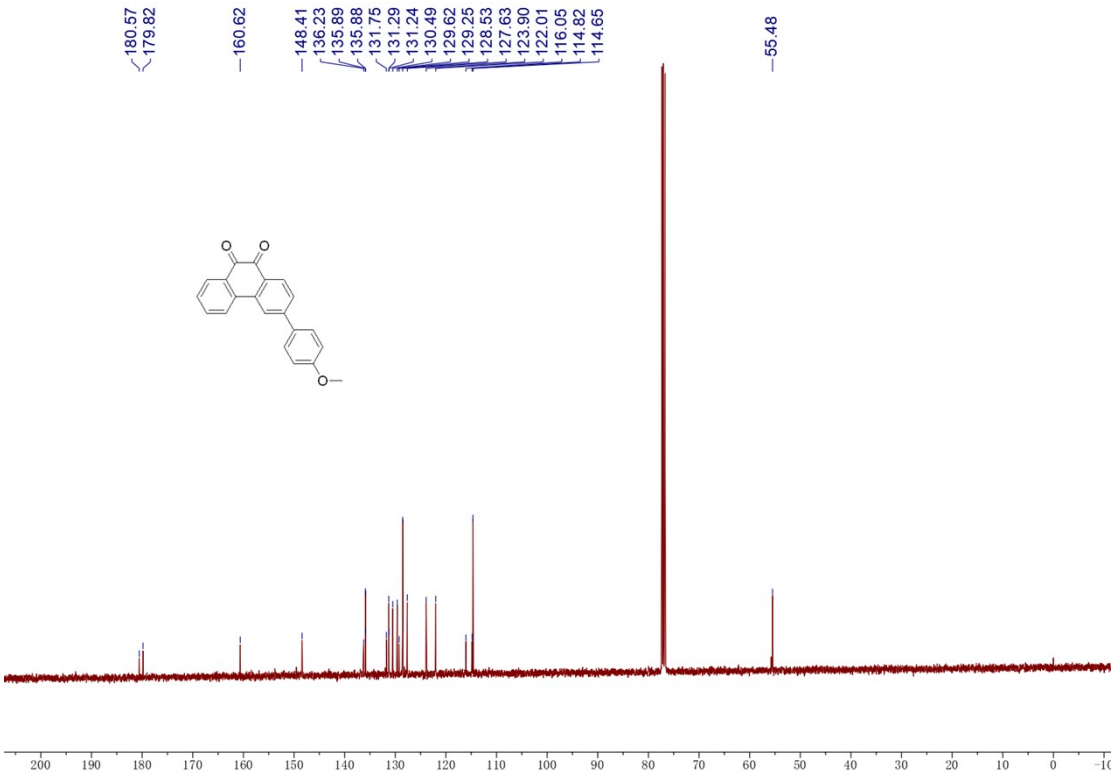

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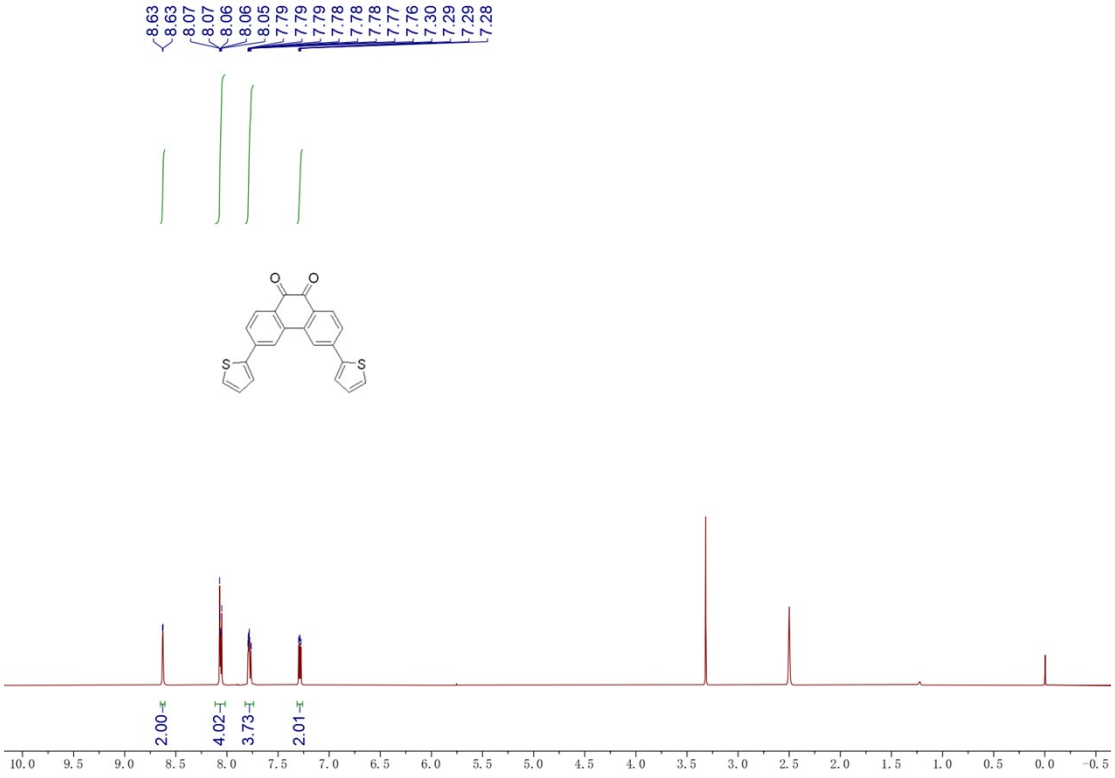

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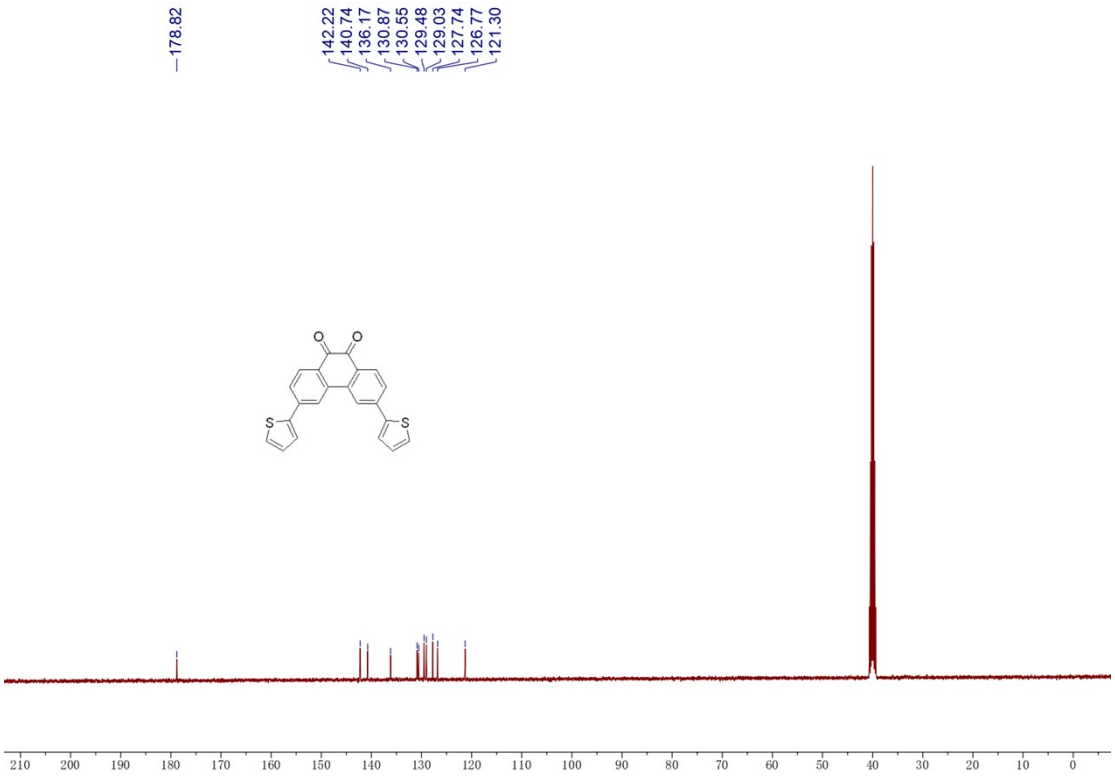

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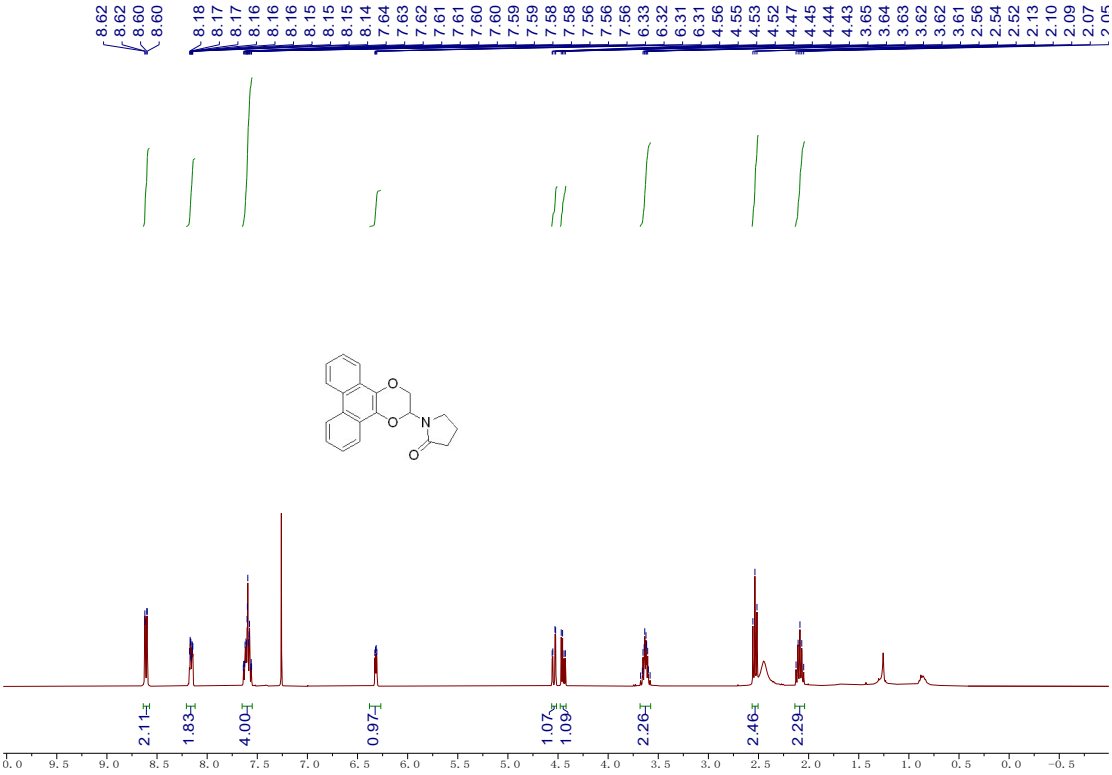

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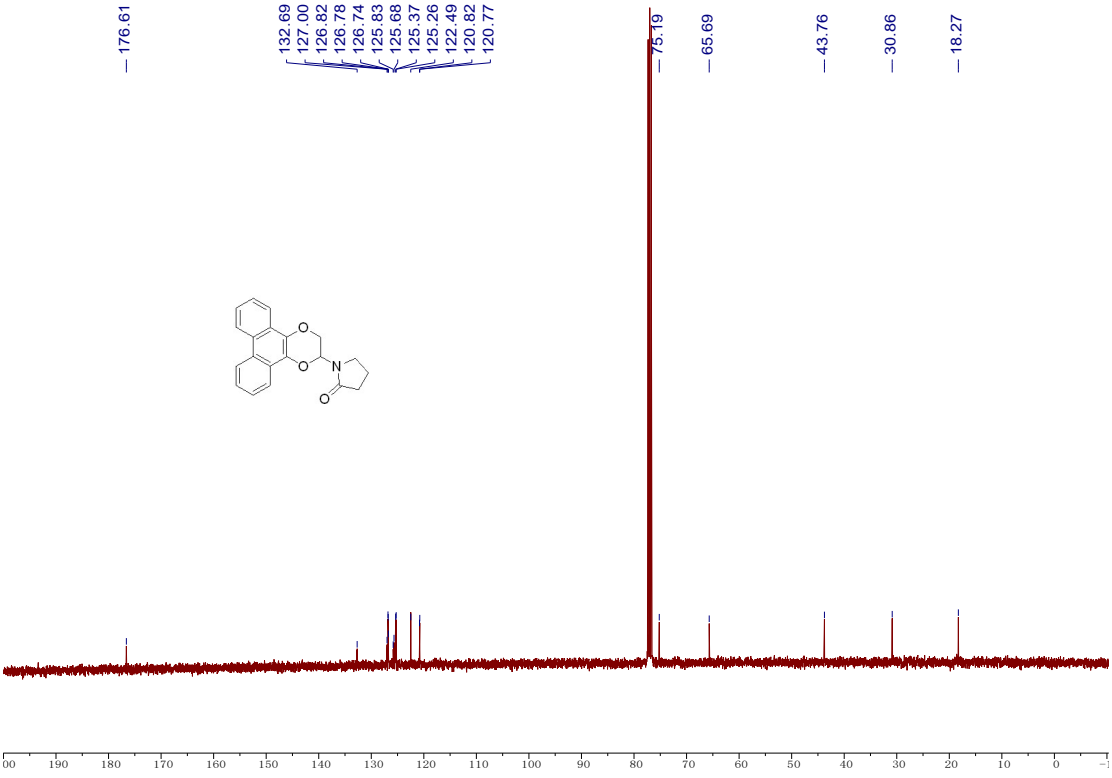

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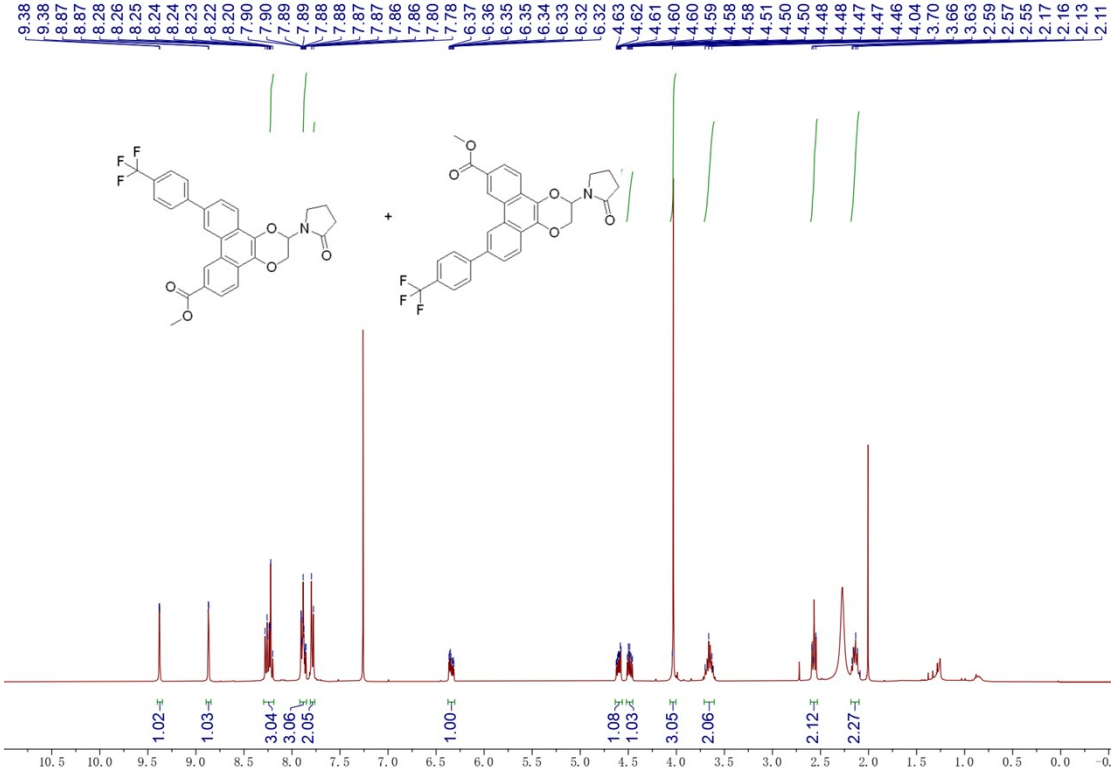

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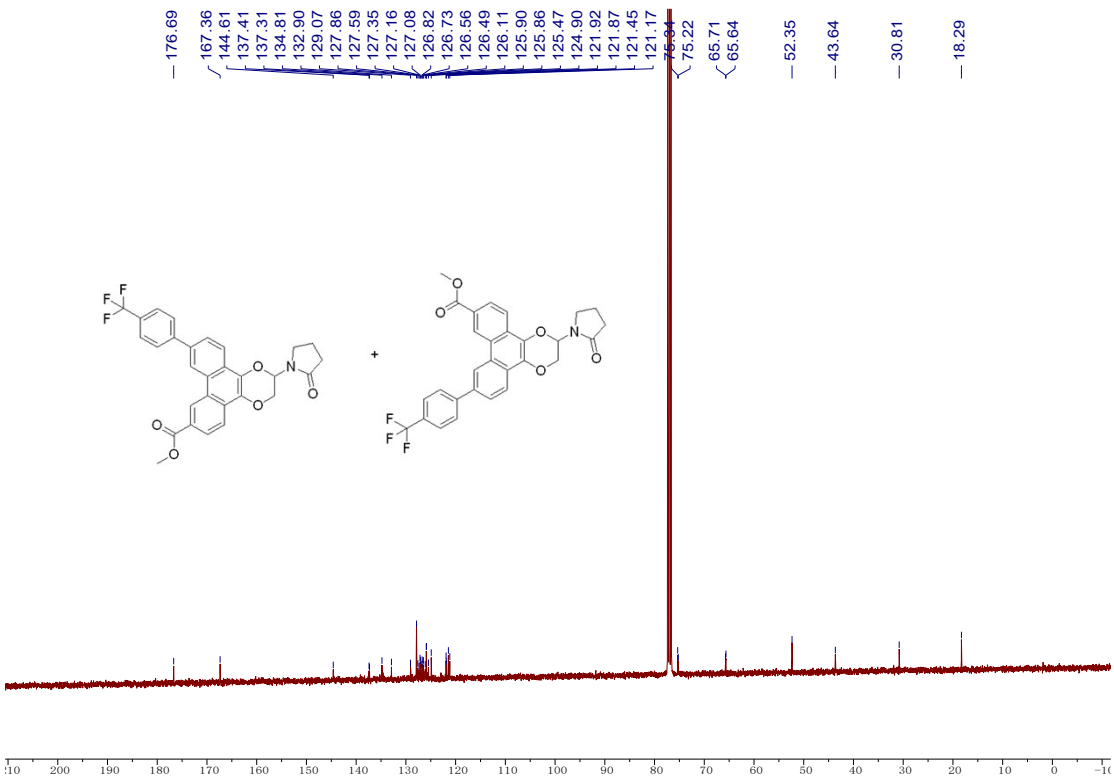

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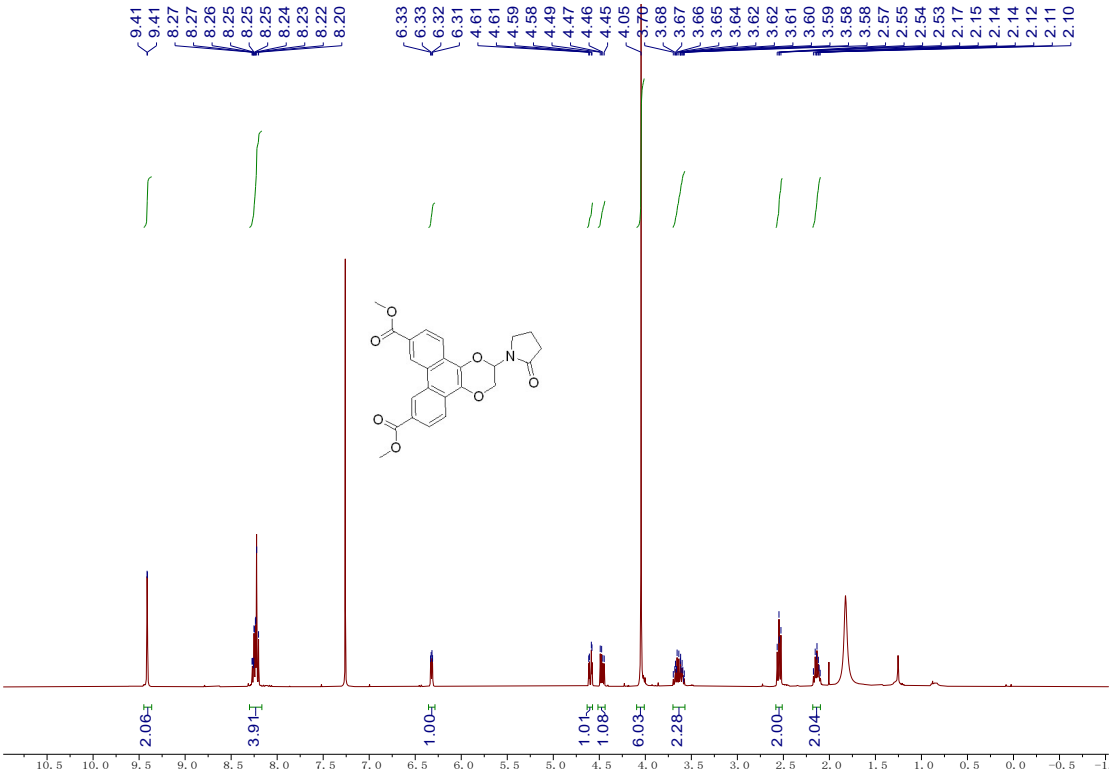

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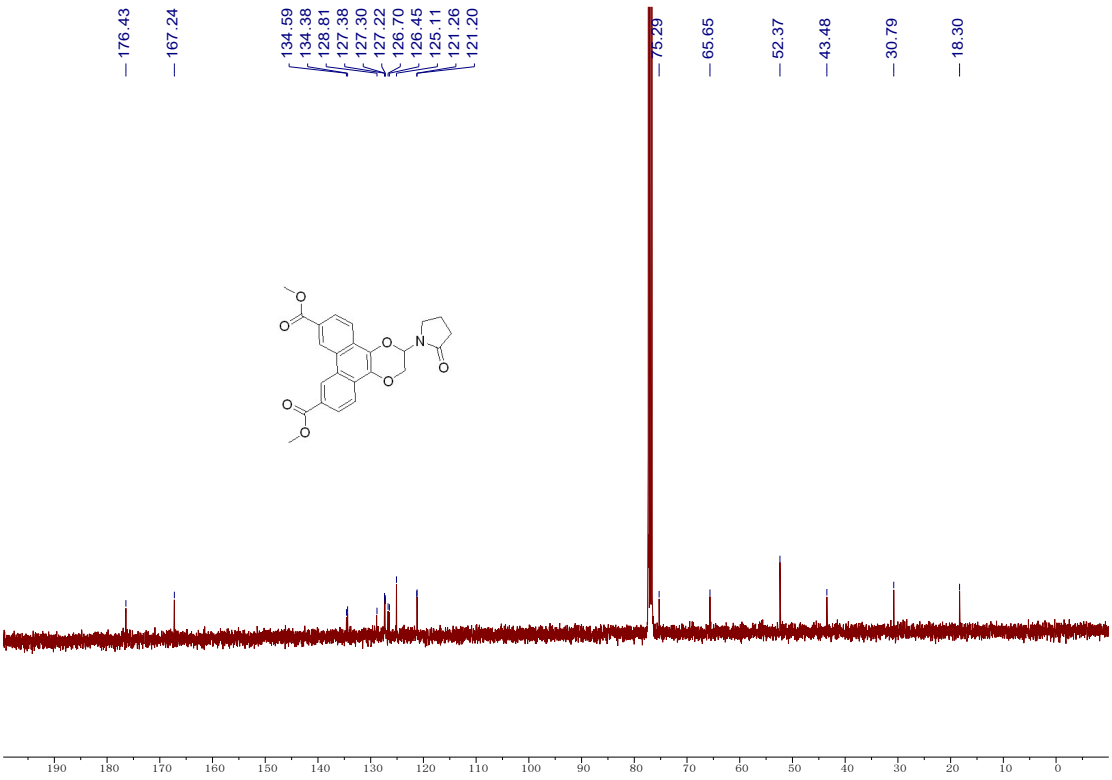

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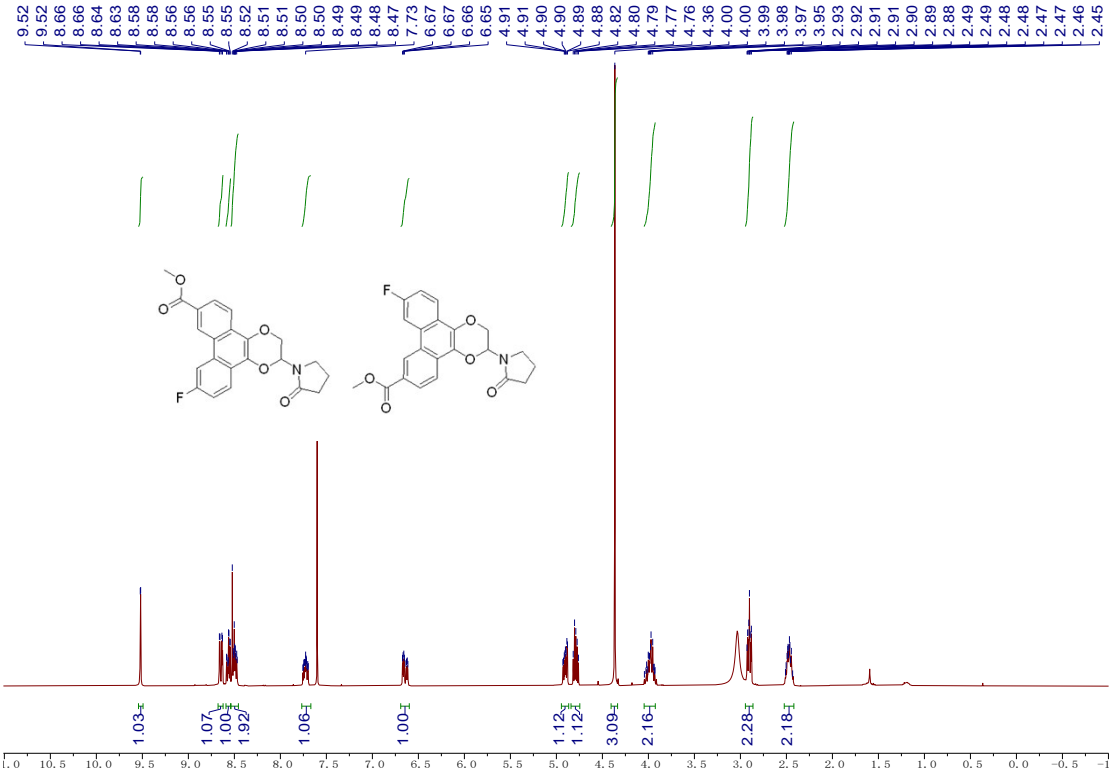

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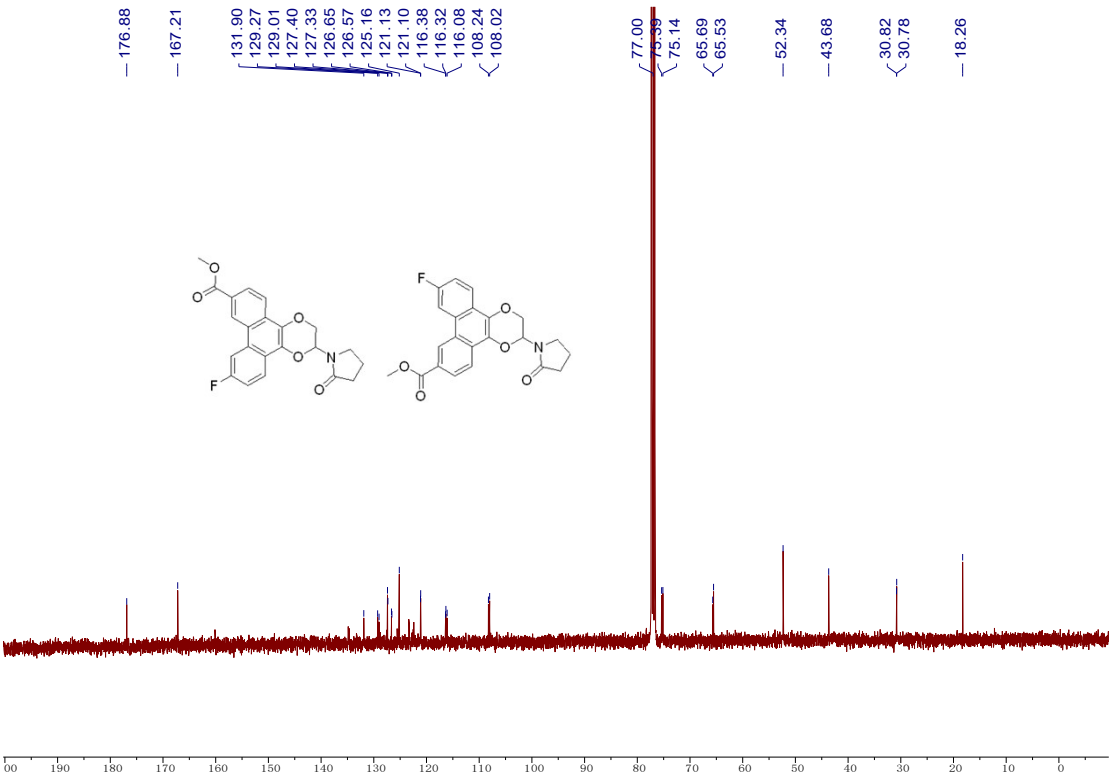

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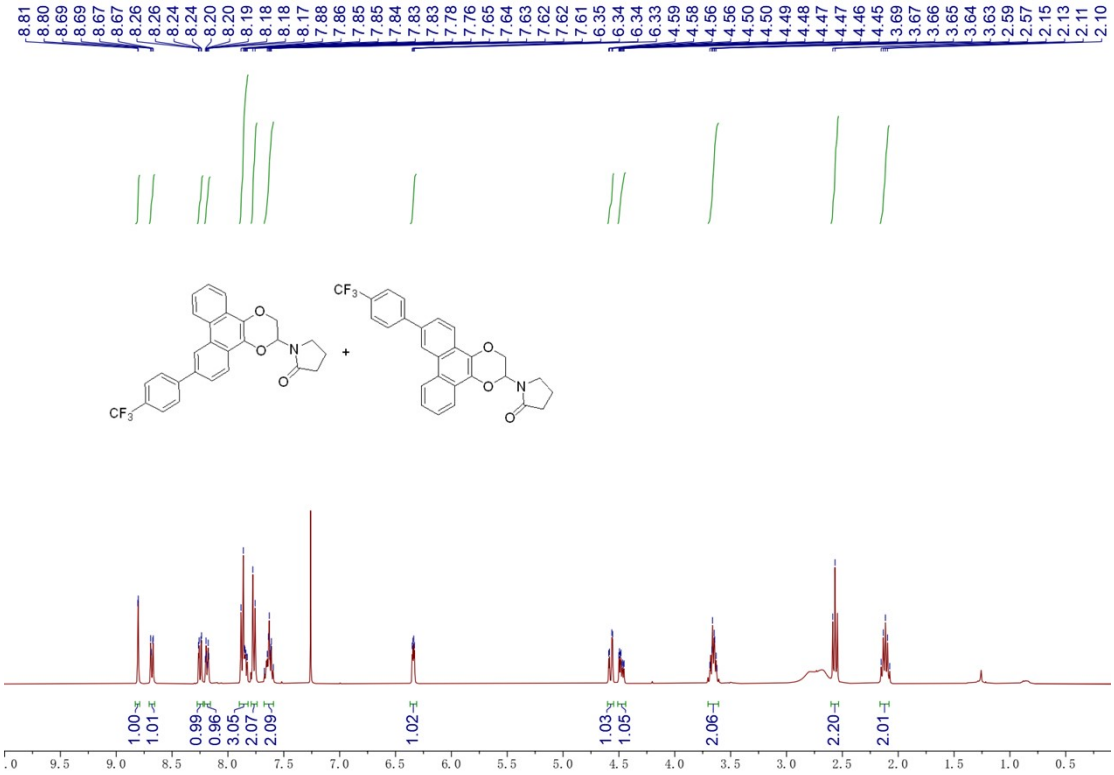

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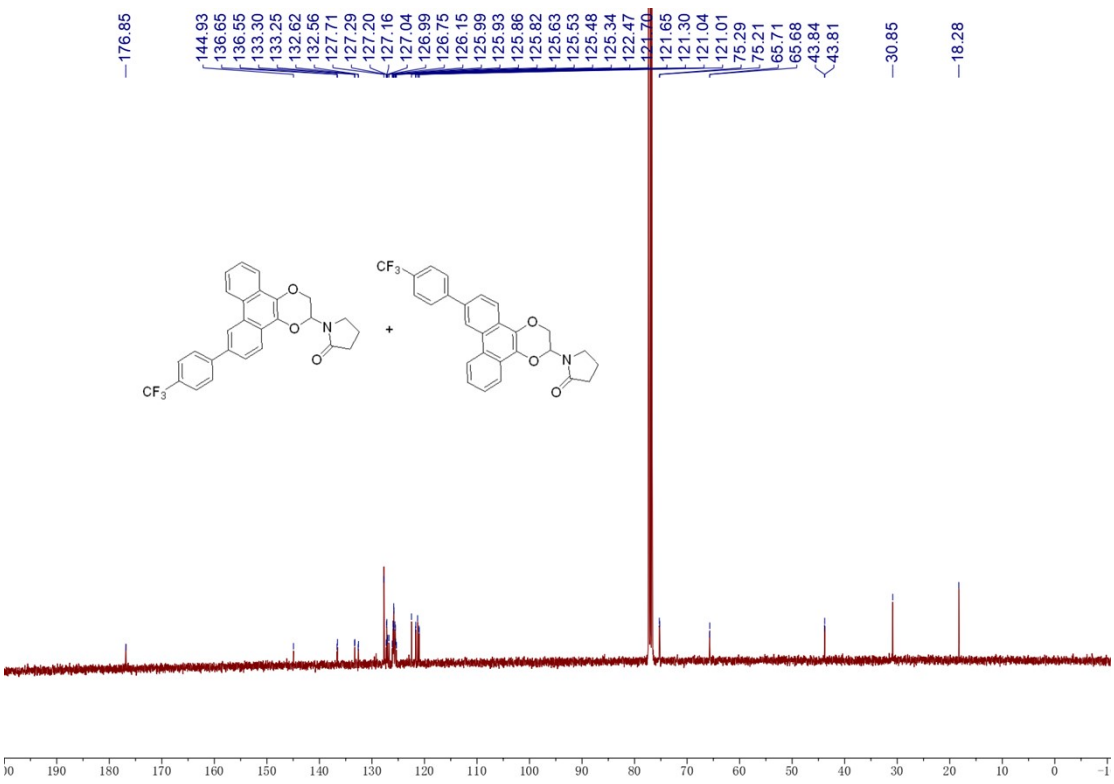

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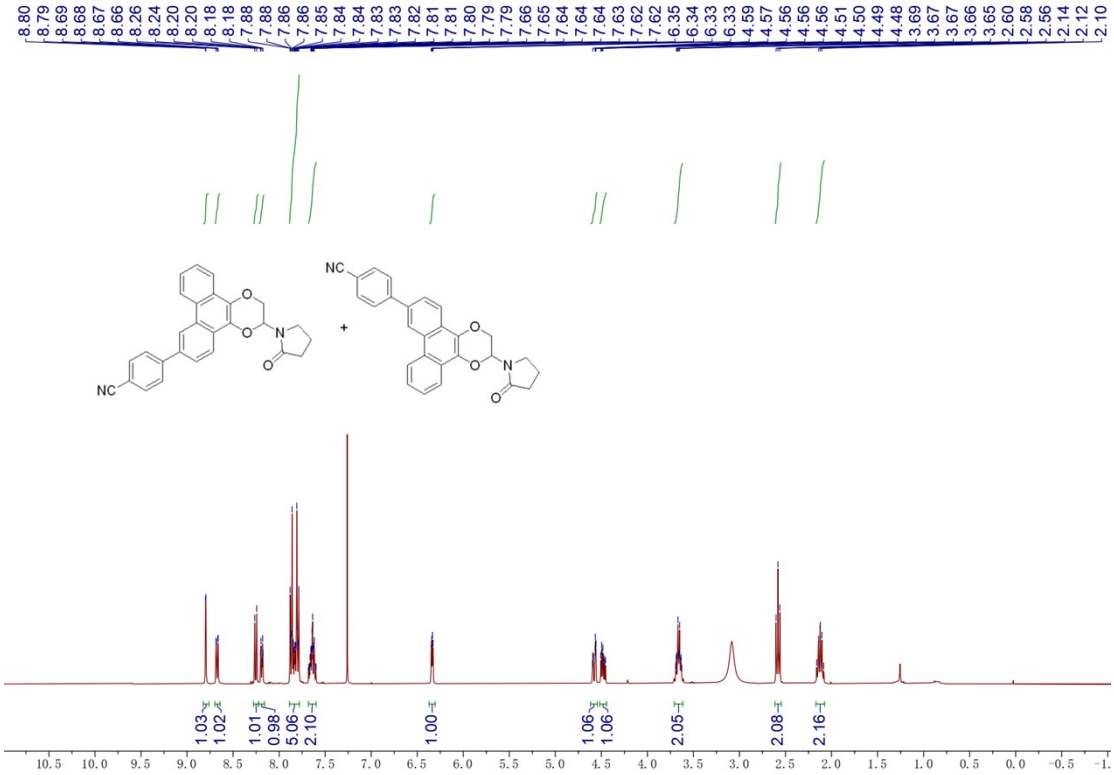

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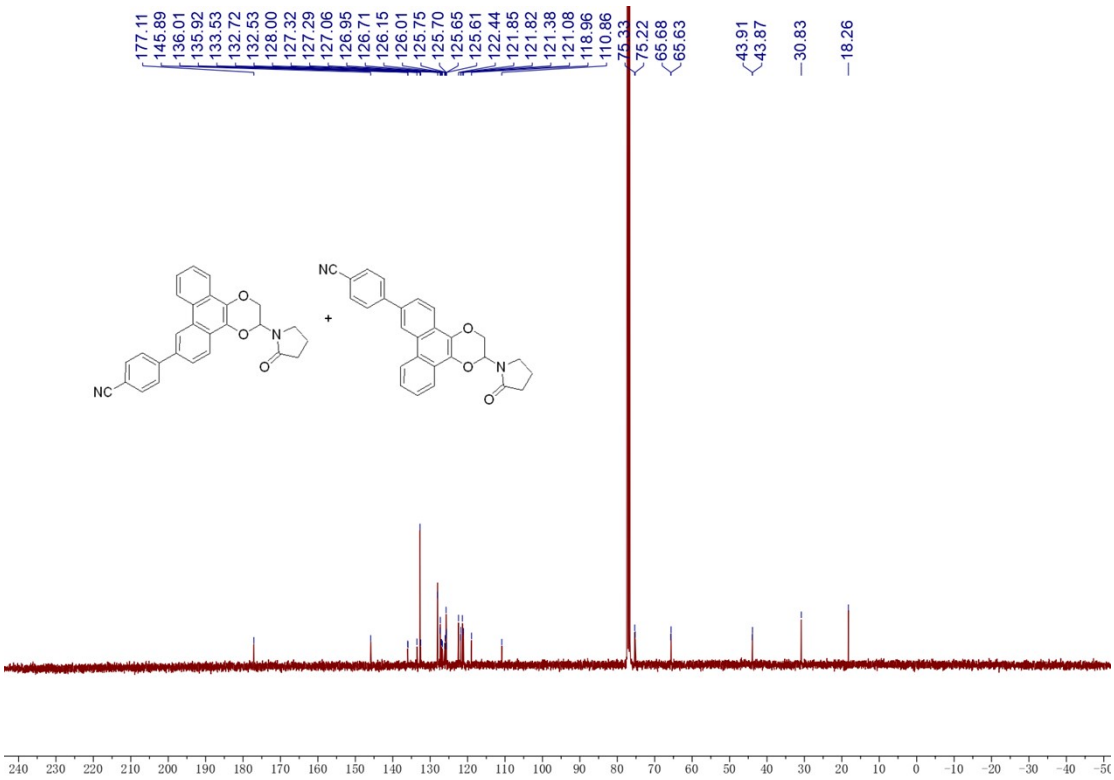

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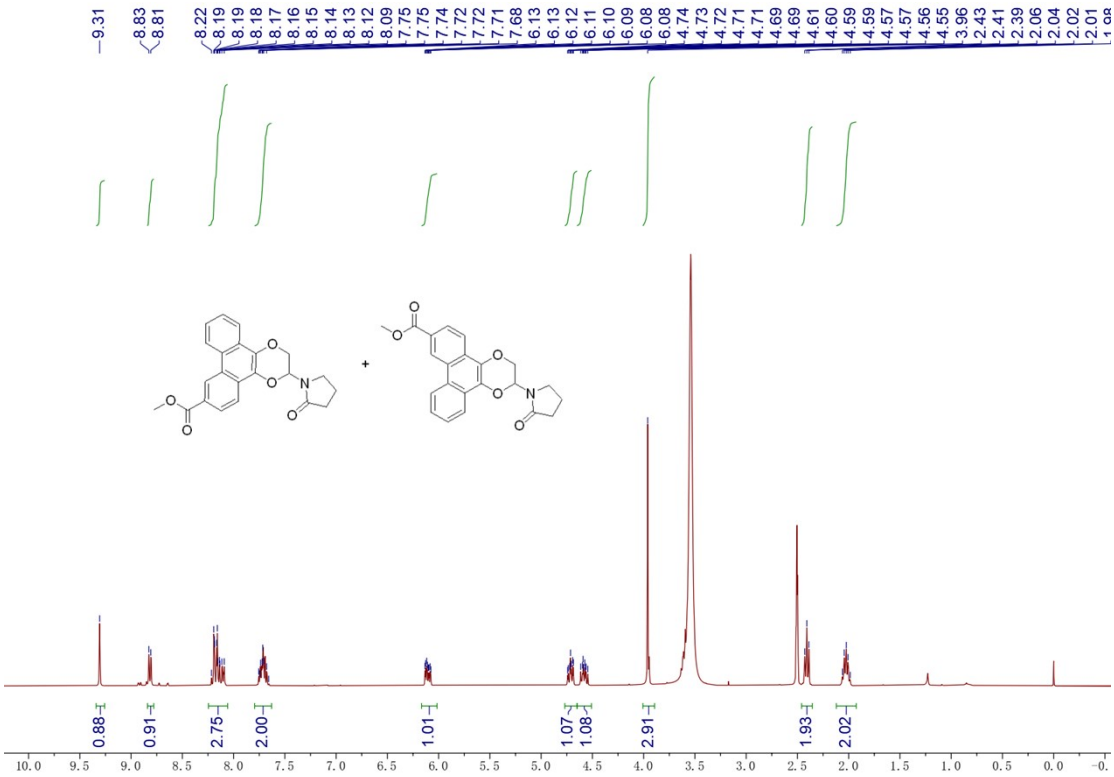

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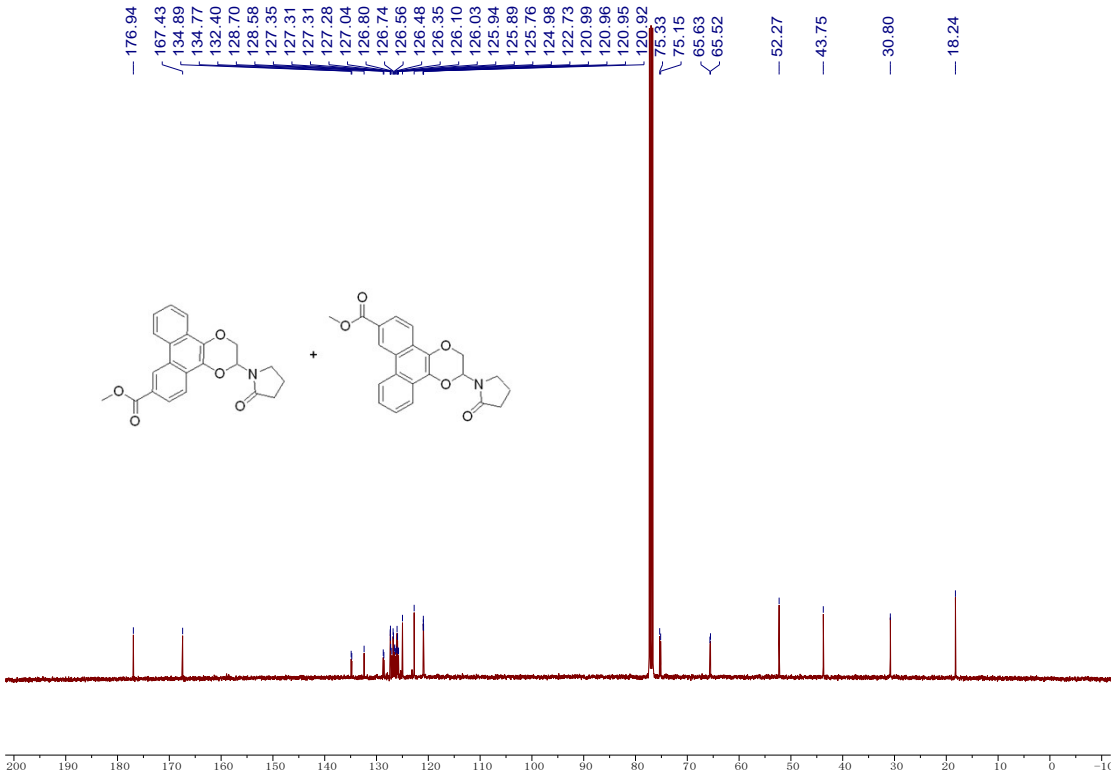

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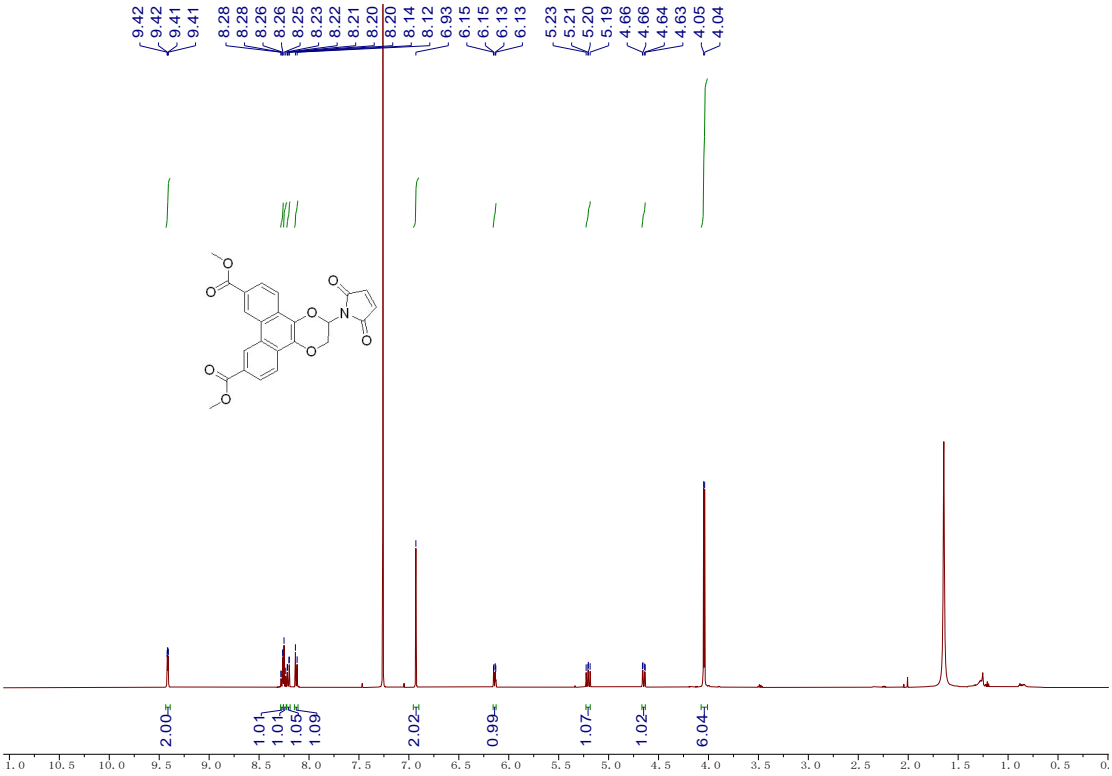
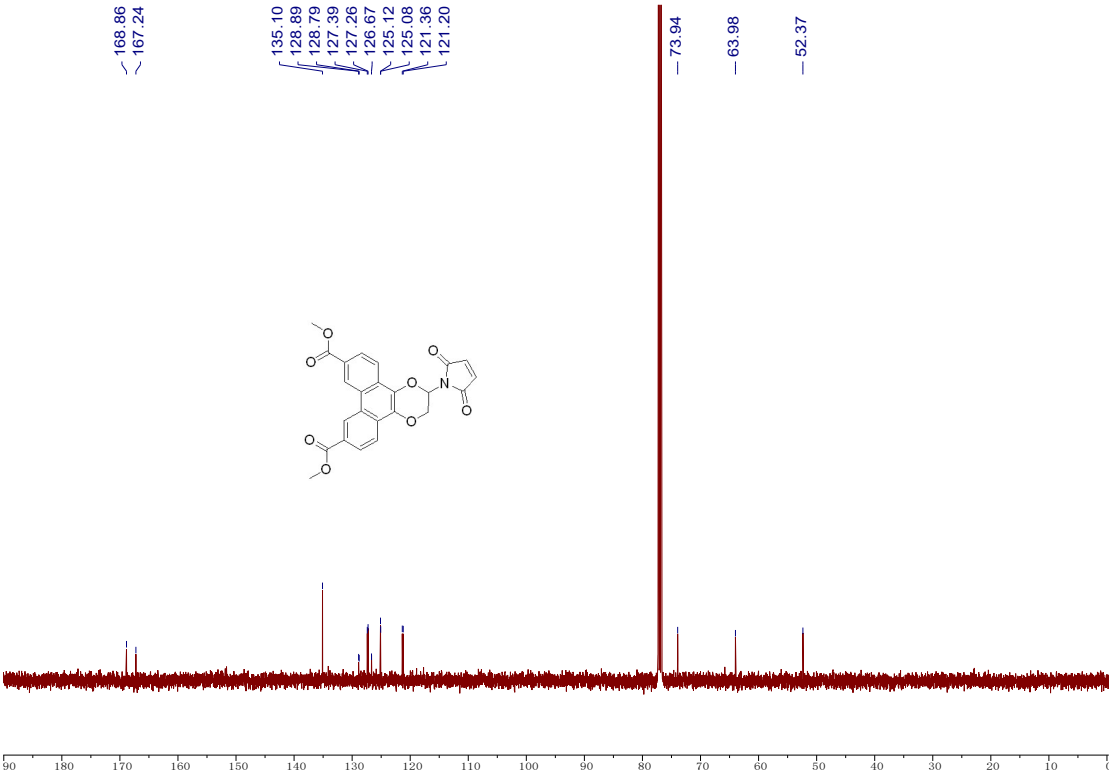
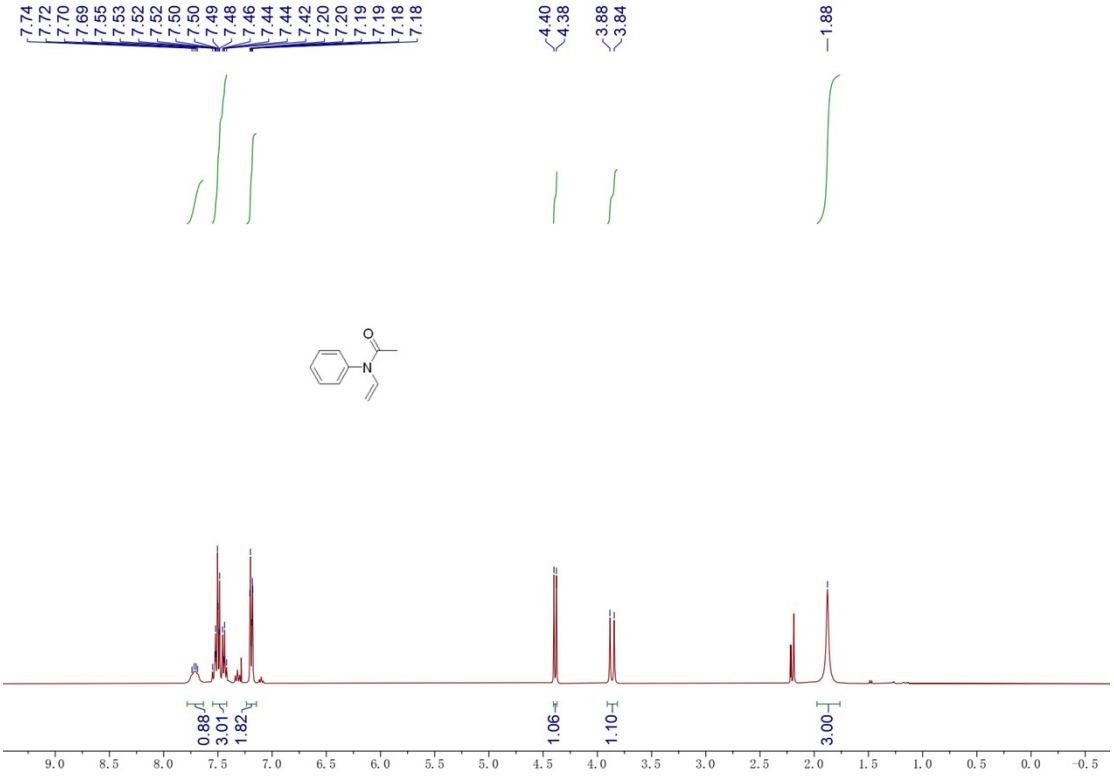


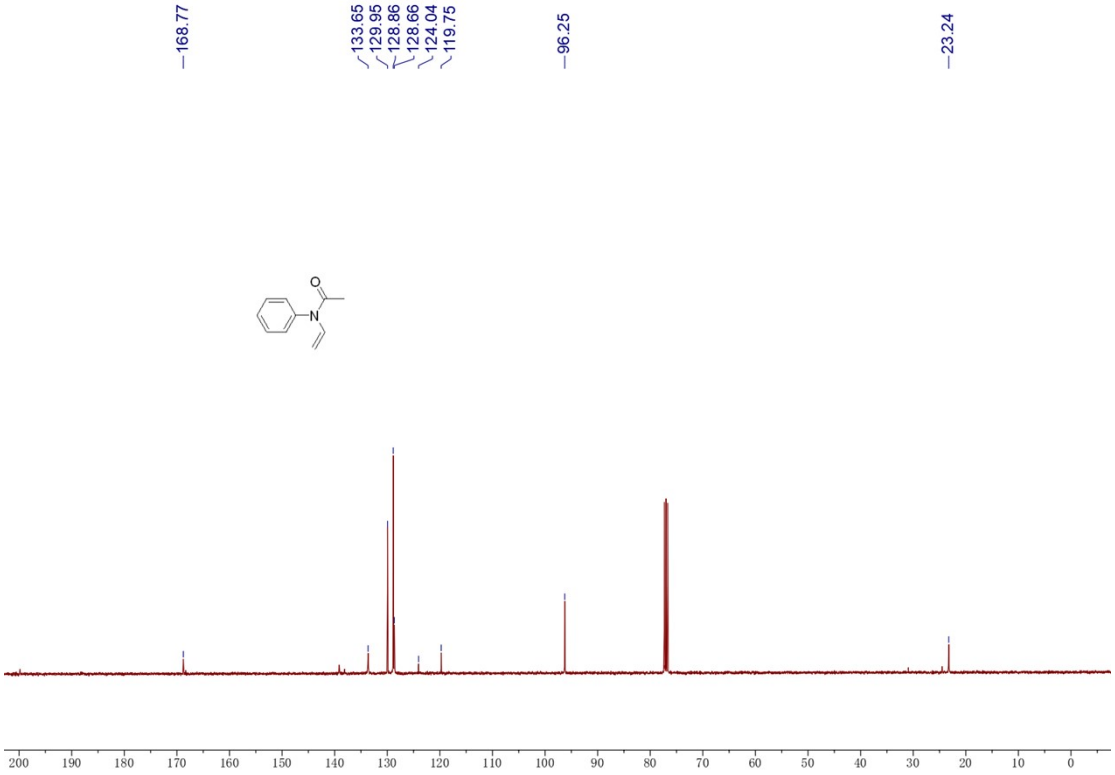
^{12}C NMR of PQ2-NVM



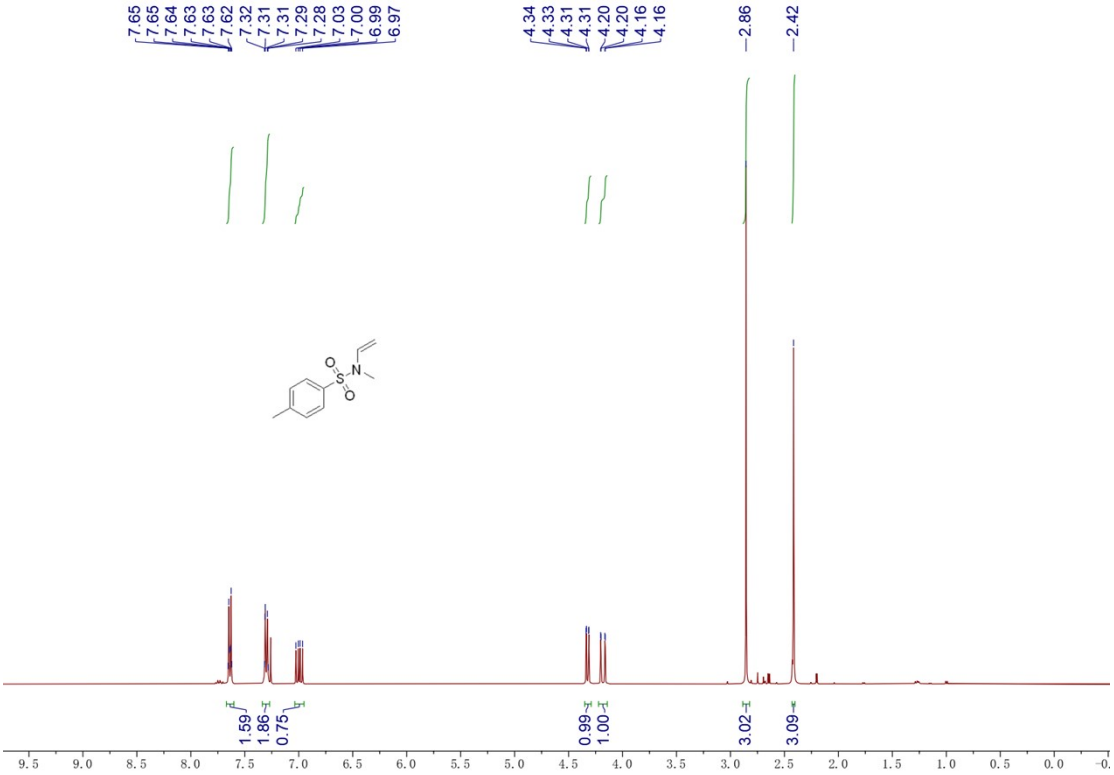
^{1}H NMR of N2



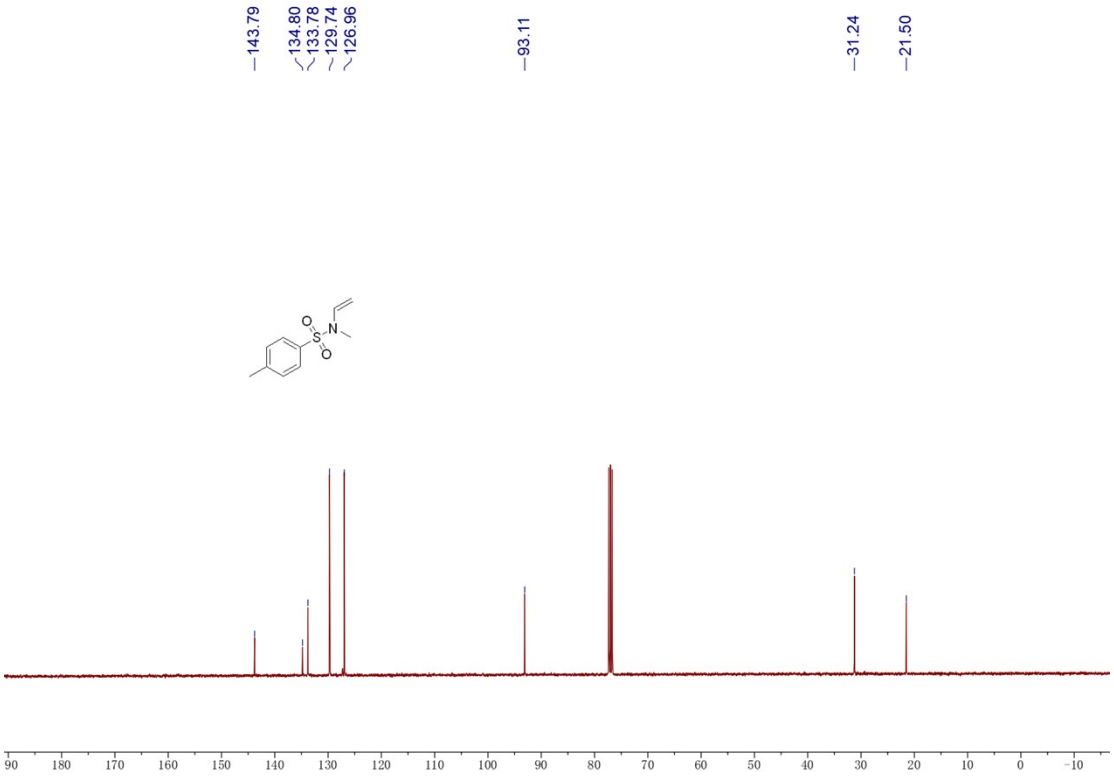
^{12}C NMR of N2



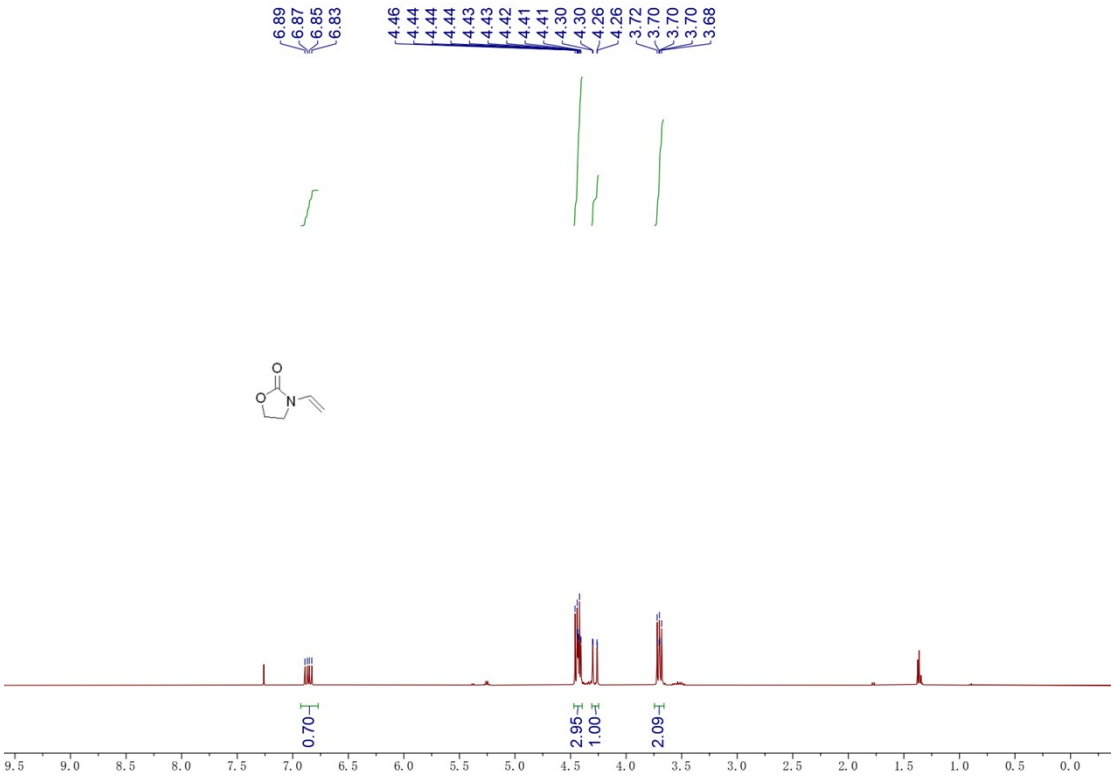
^{1}H NMR of N3



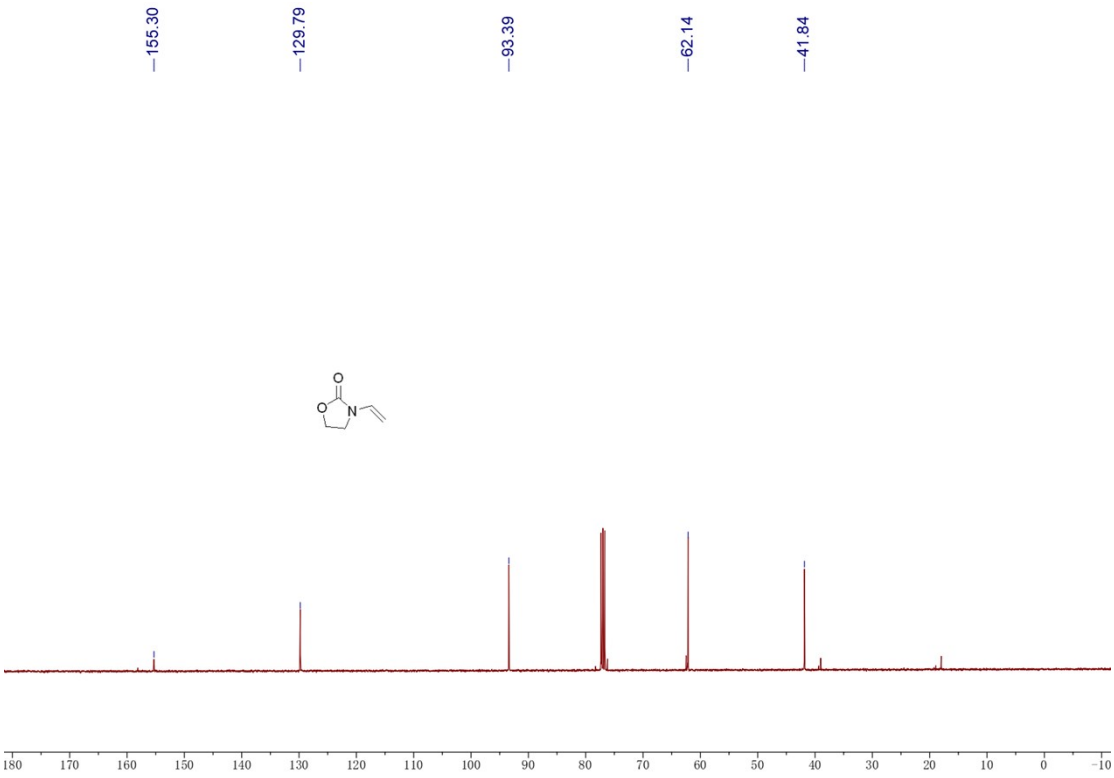
^{12}C NMR of N3



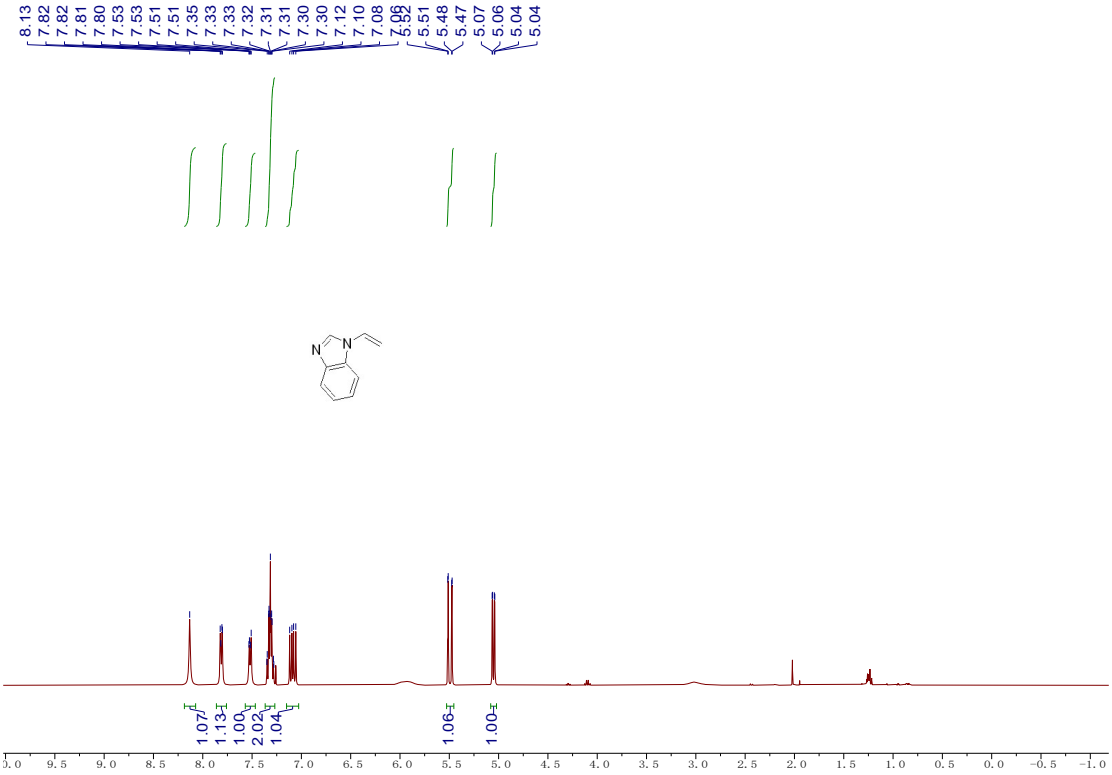
^{1}H NMR of N4



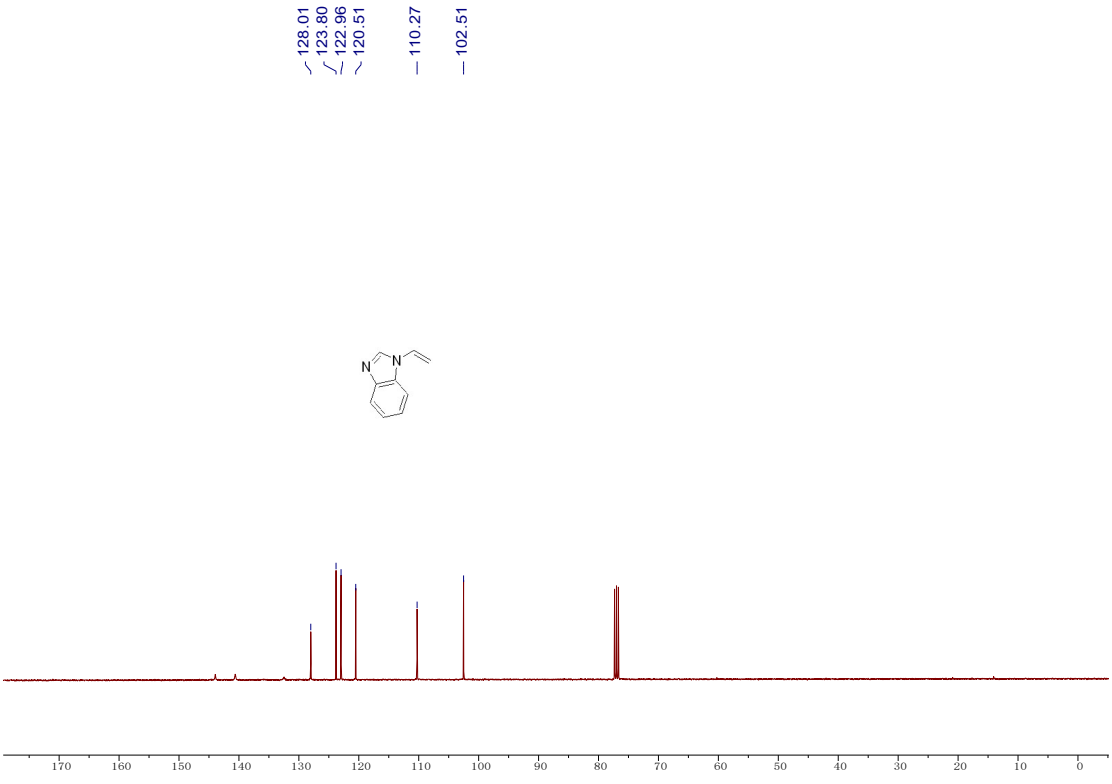
^{12}C NMR of N4



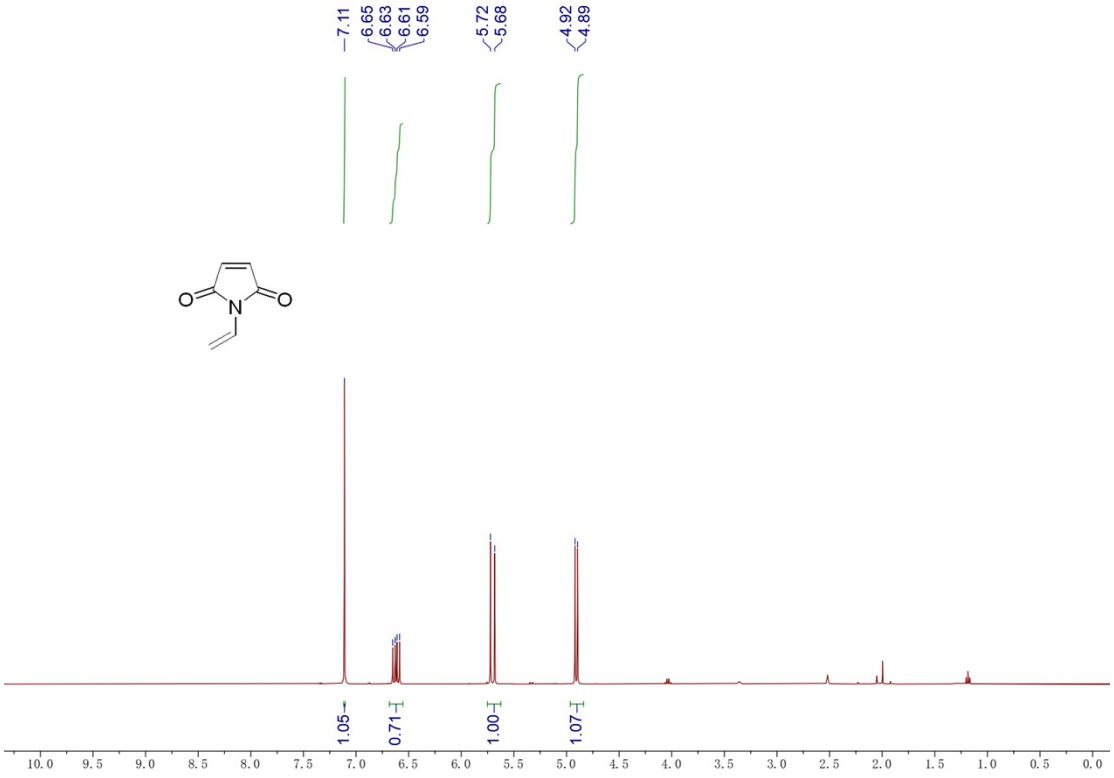
^{1}H NMR of N6



^{12}C NMR of N6



^{1}H NMR of NVM



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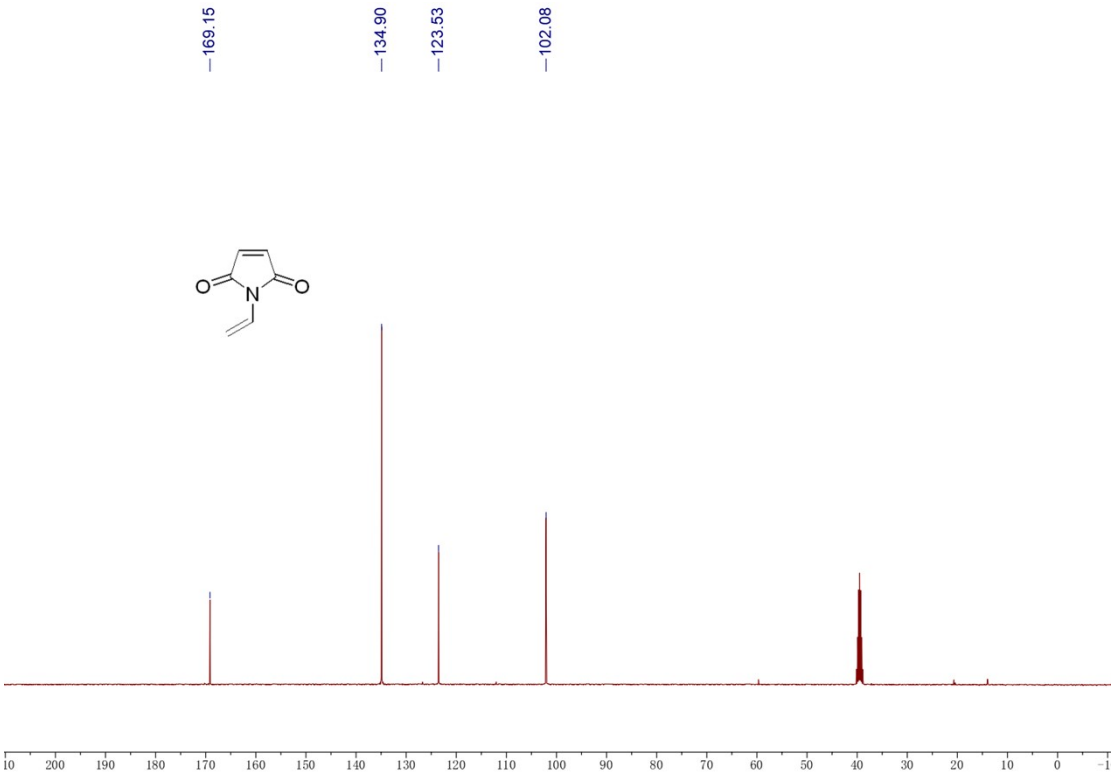
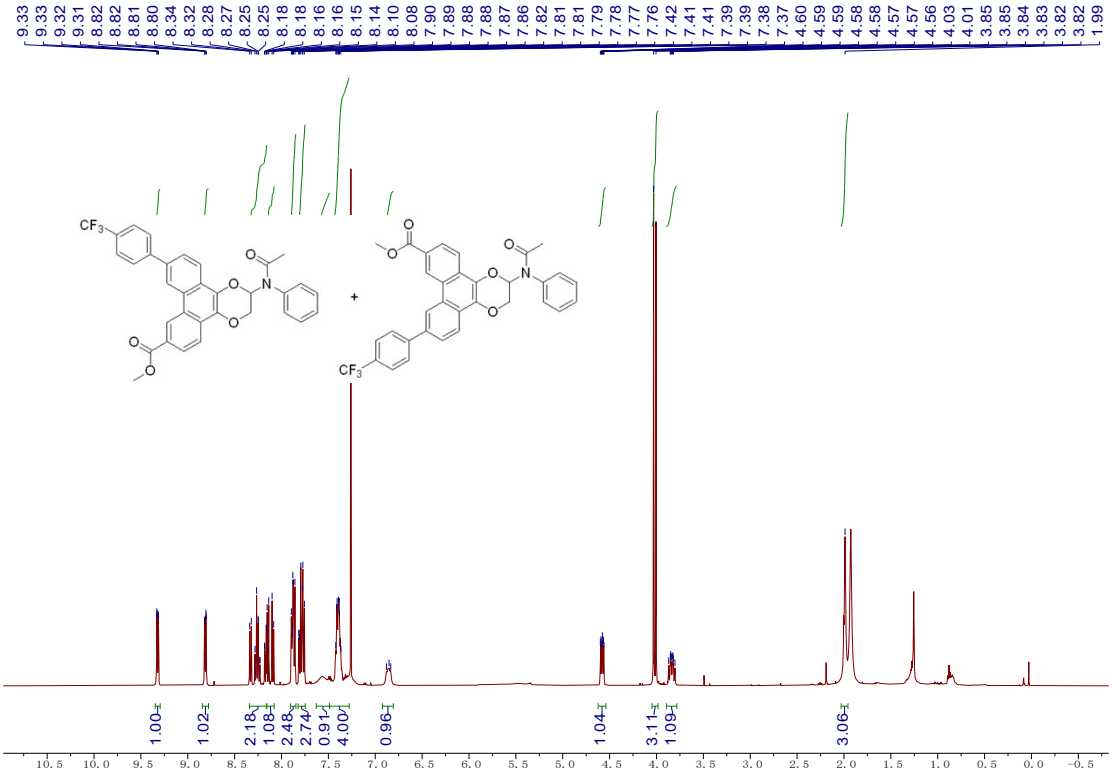
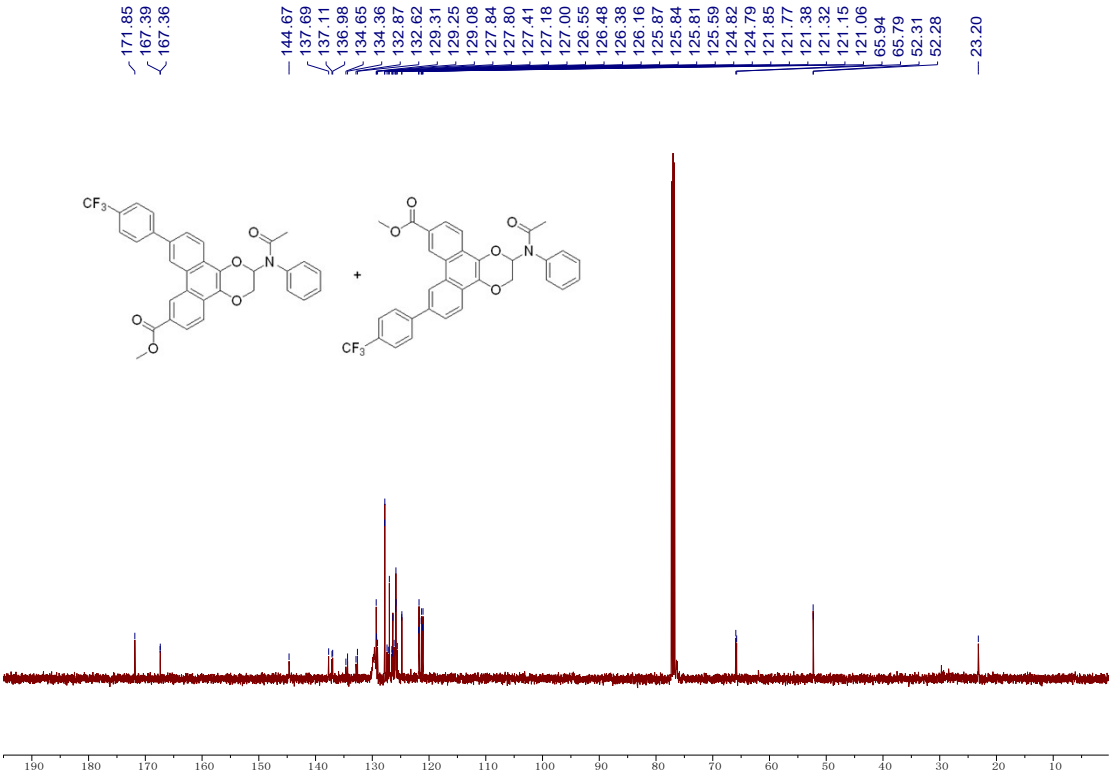


^{1}H NMR of PQ1-N2



^{12}C NMR of PQ1-N2



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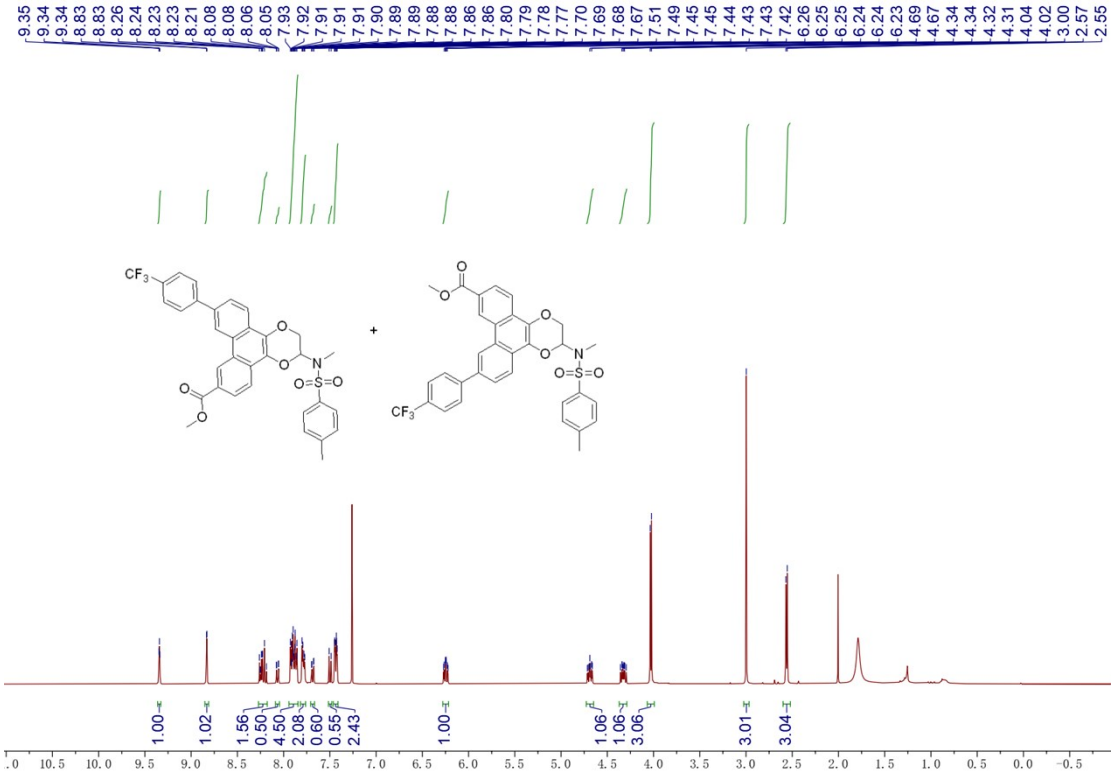
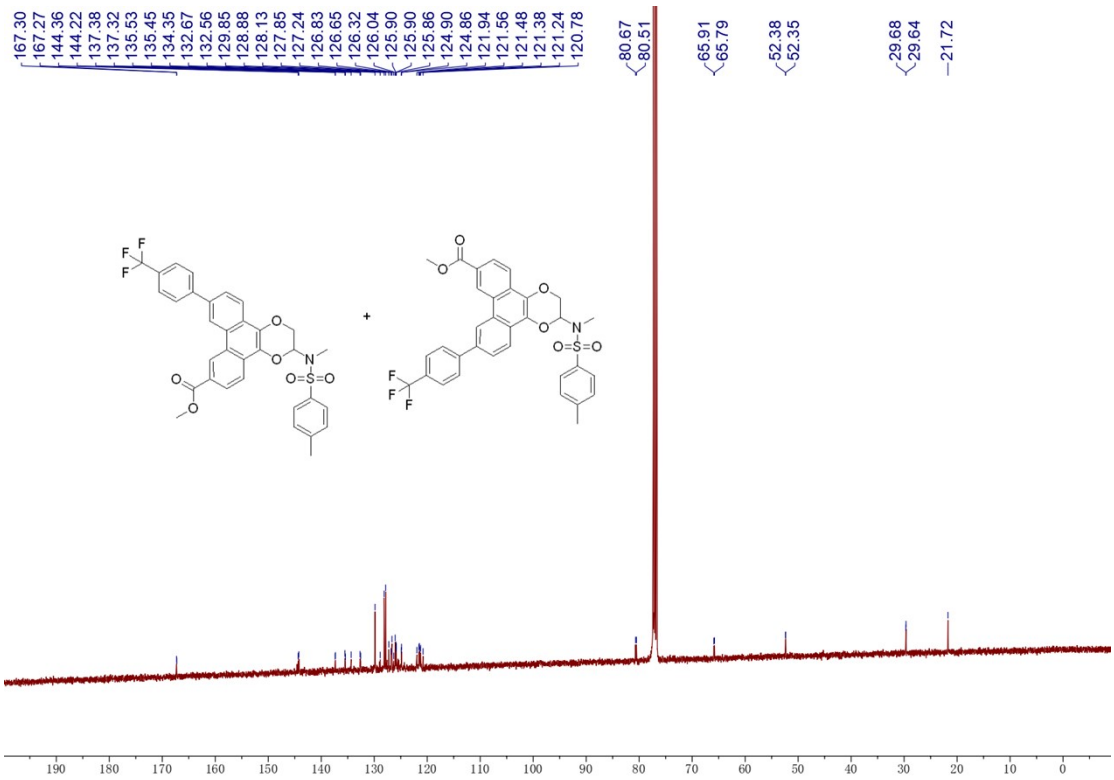
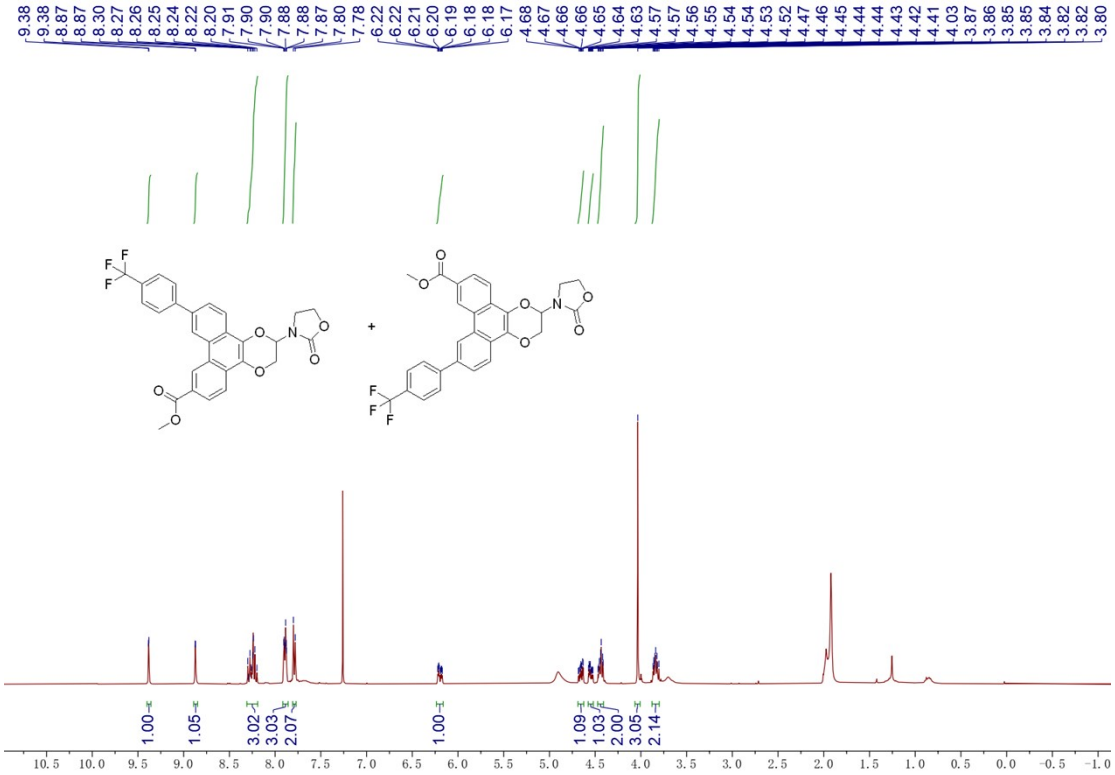


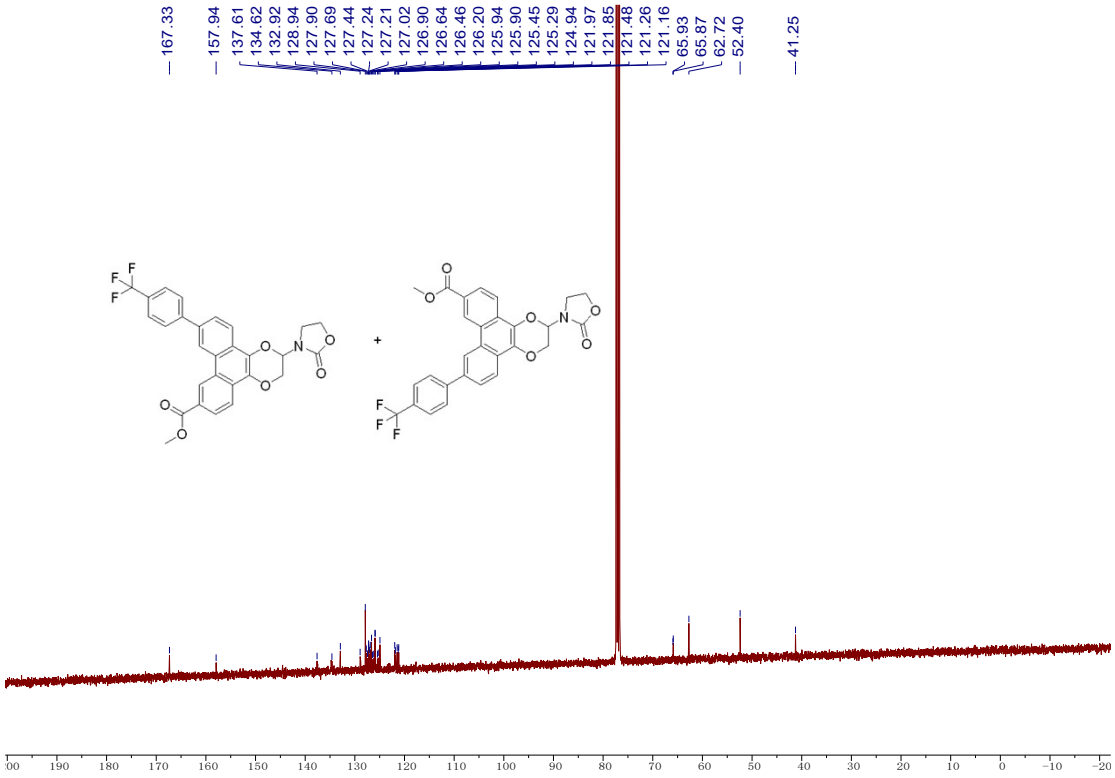
^{12}C NMR of PQ1-N3



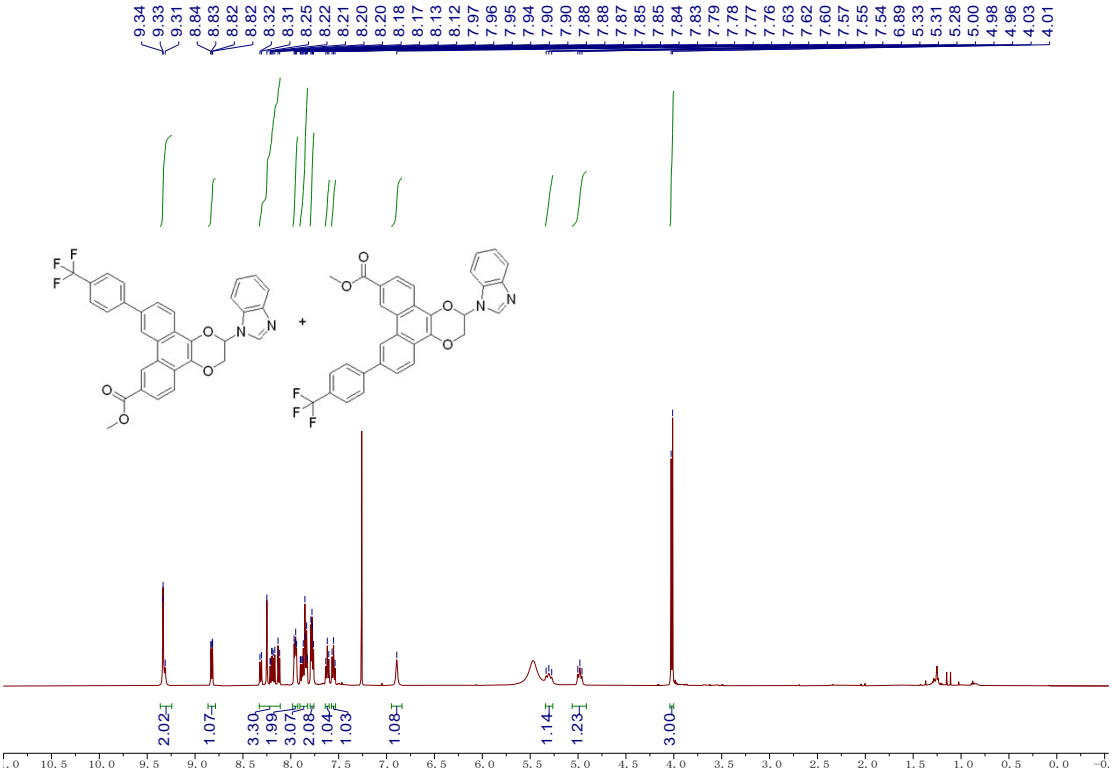
^{1}H NMR of PQ1-N4



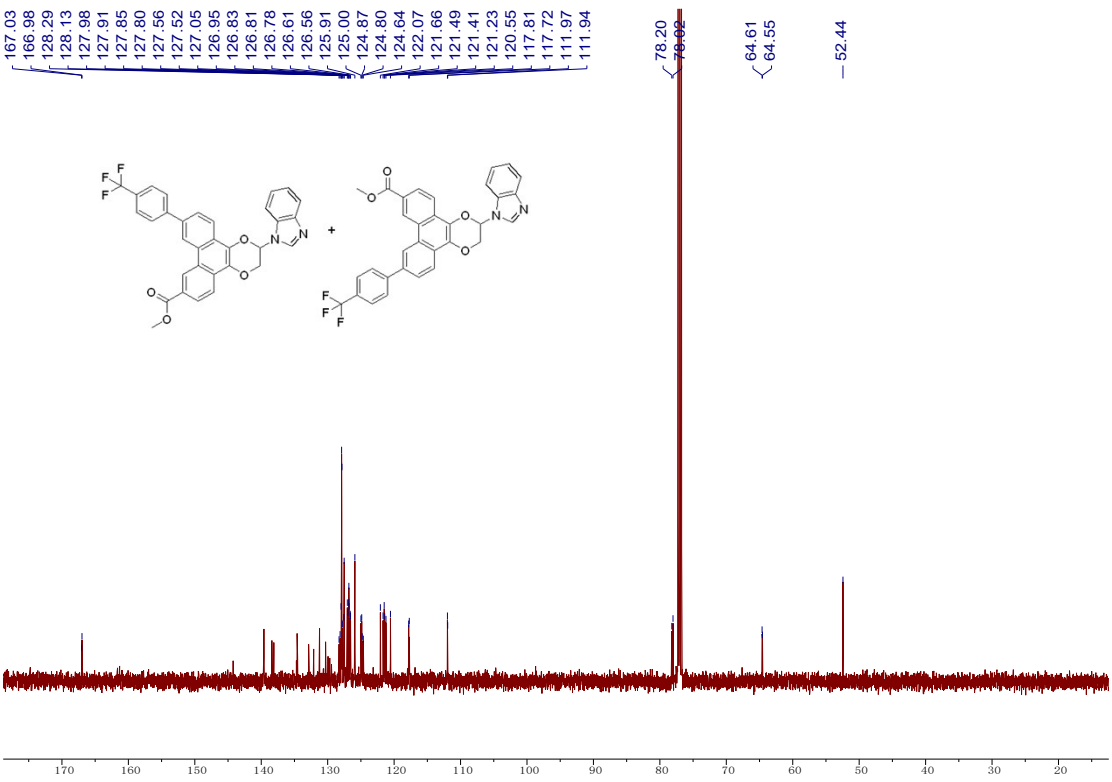
^{12}C NMR of PQ1-N4



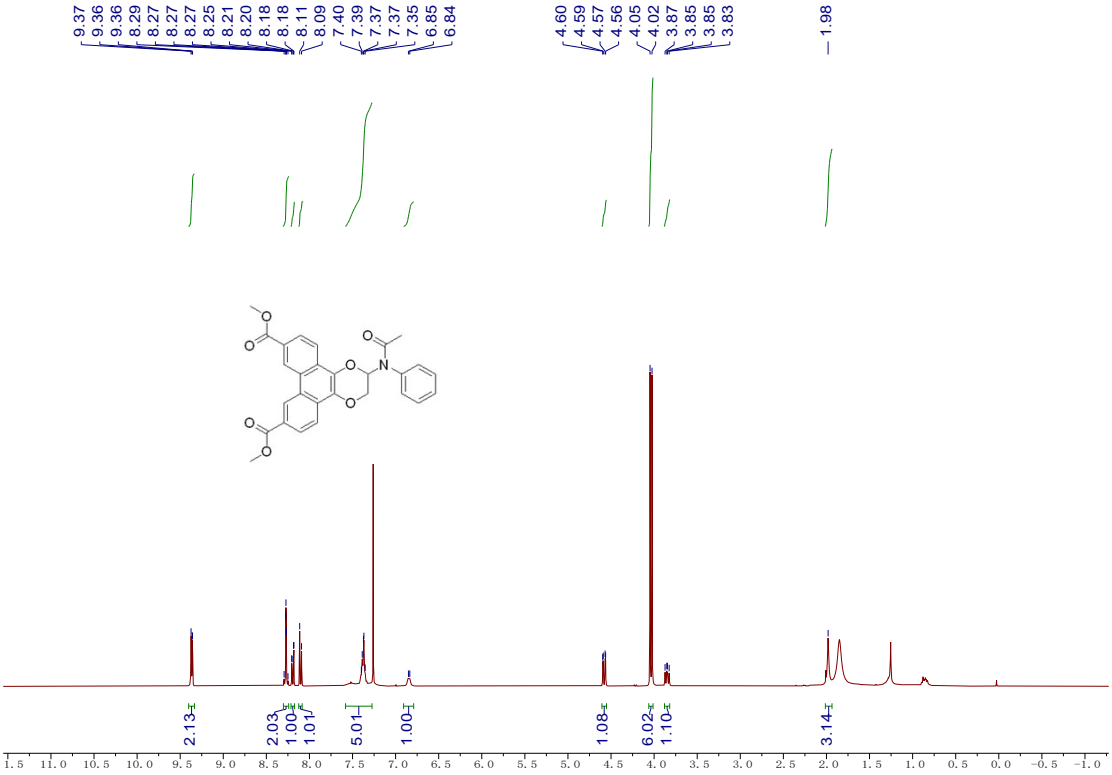
^{1}H NMR of PQ1-N6



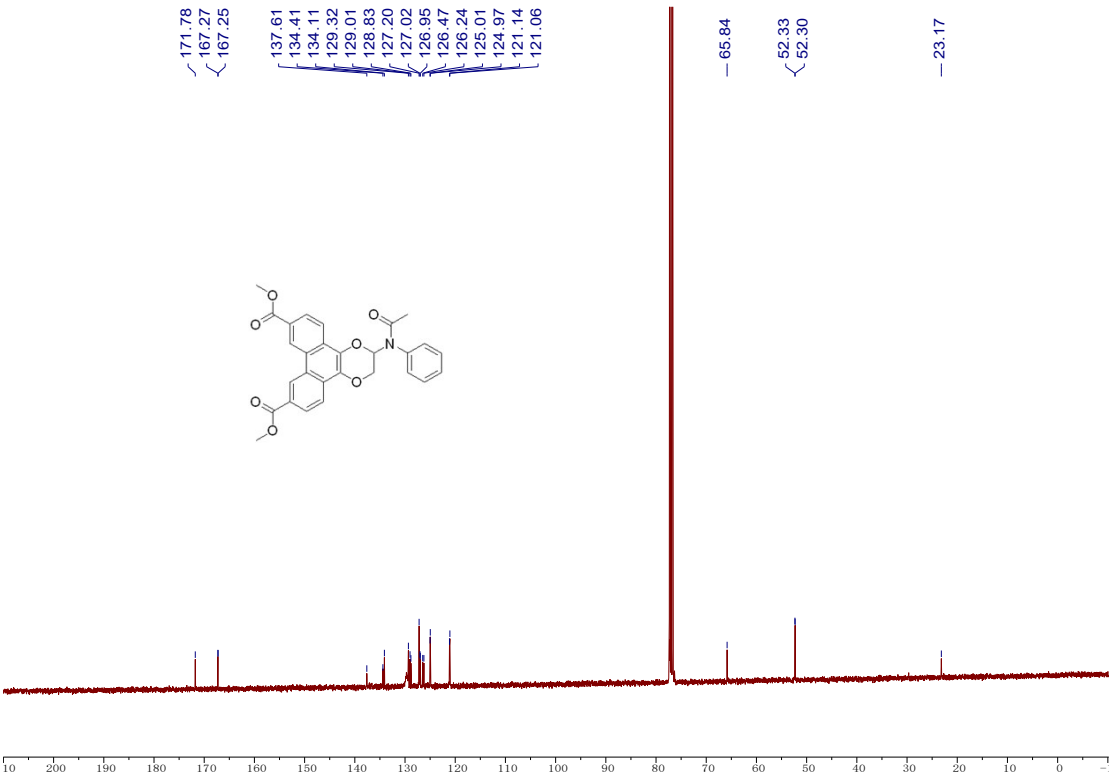
^{12}C NMR of PQ1-N6



^{1}H NMR of PQ2-N2



^{1}H NMR of PQ2-N2



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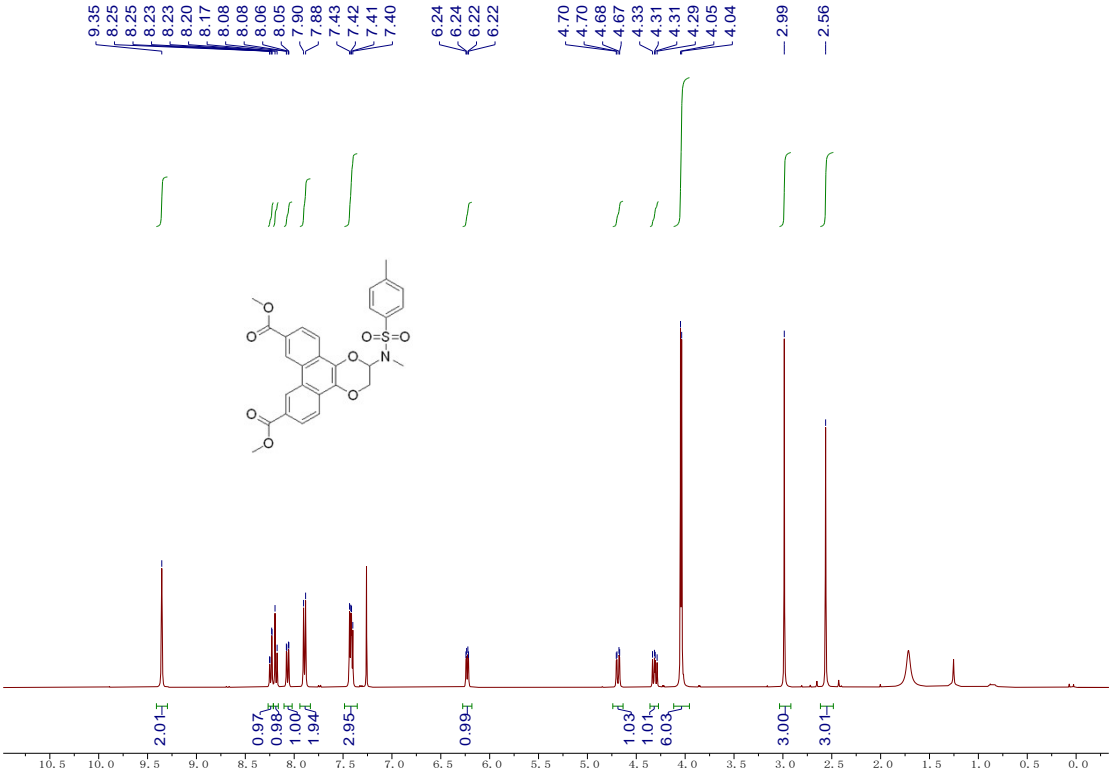
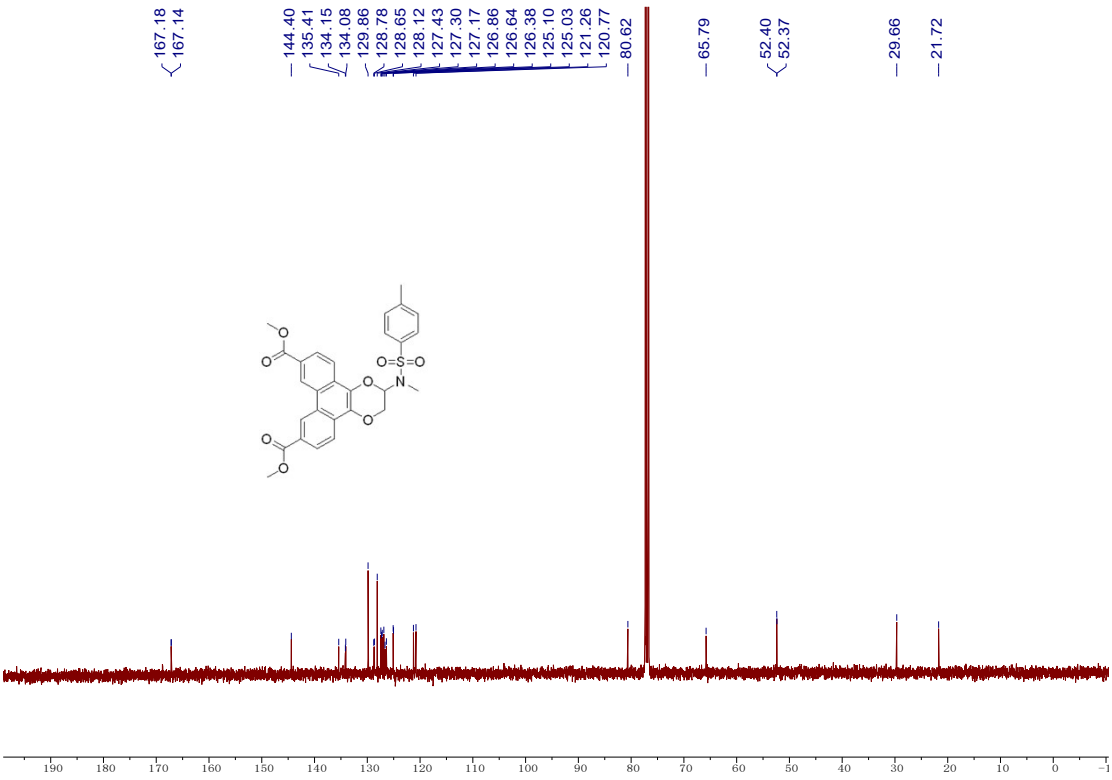
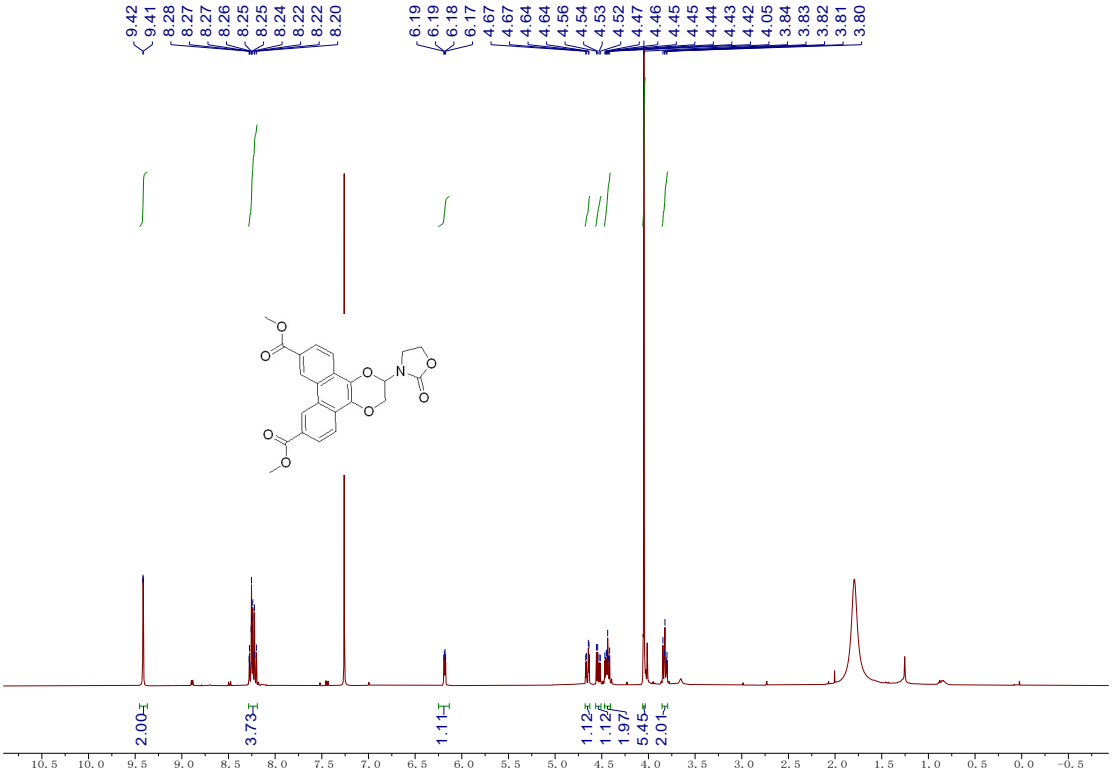


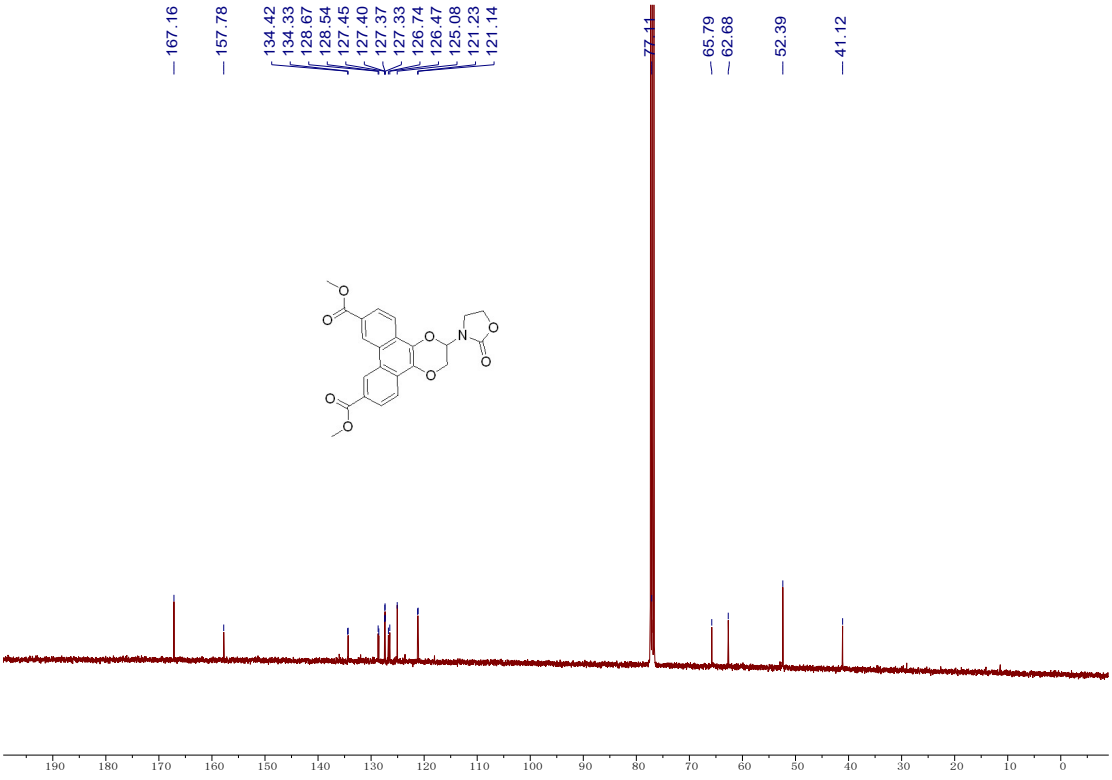
^{12}C NMR of PQ2-N3



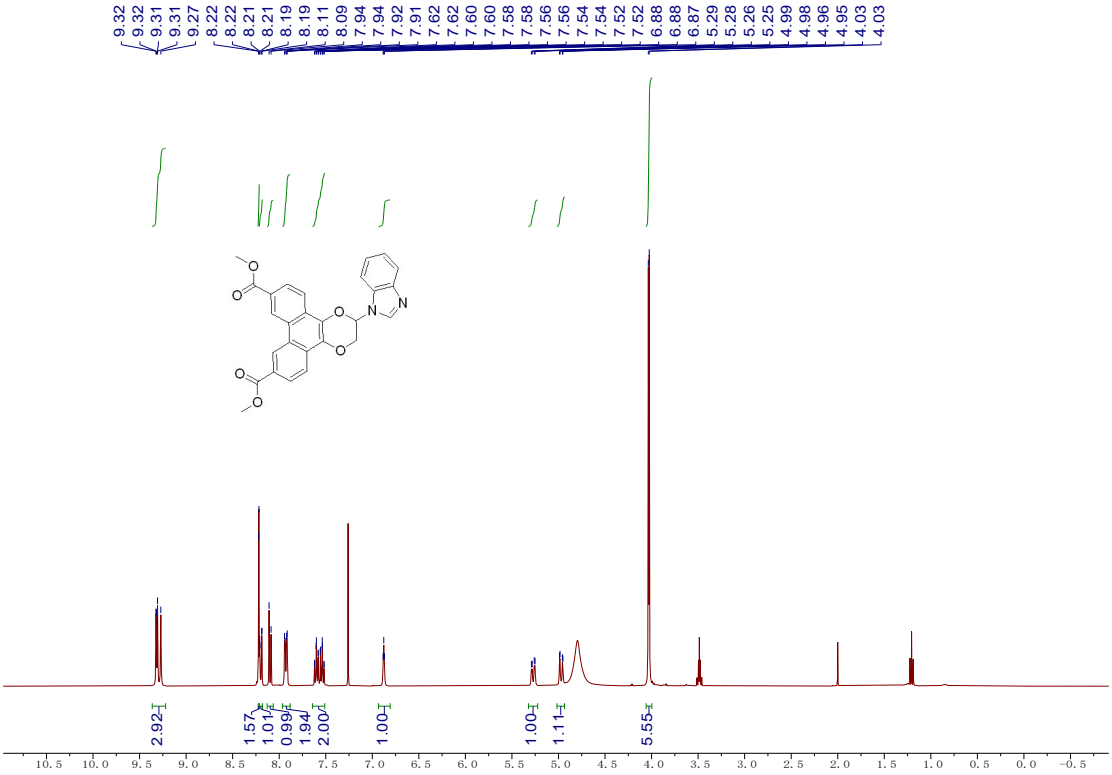
^{1}H NMR of PQ2-N4



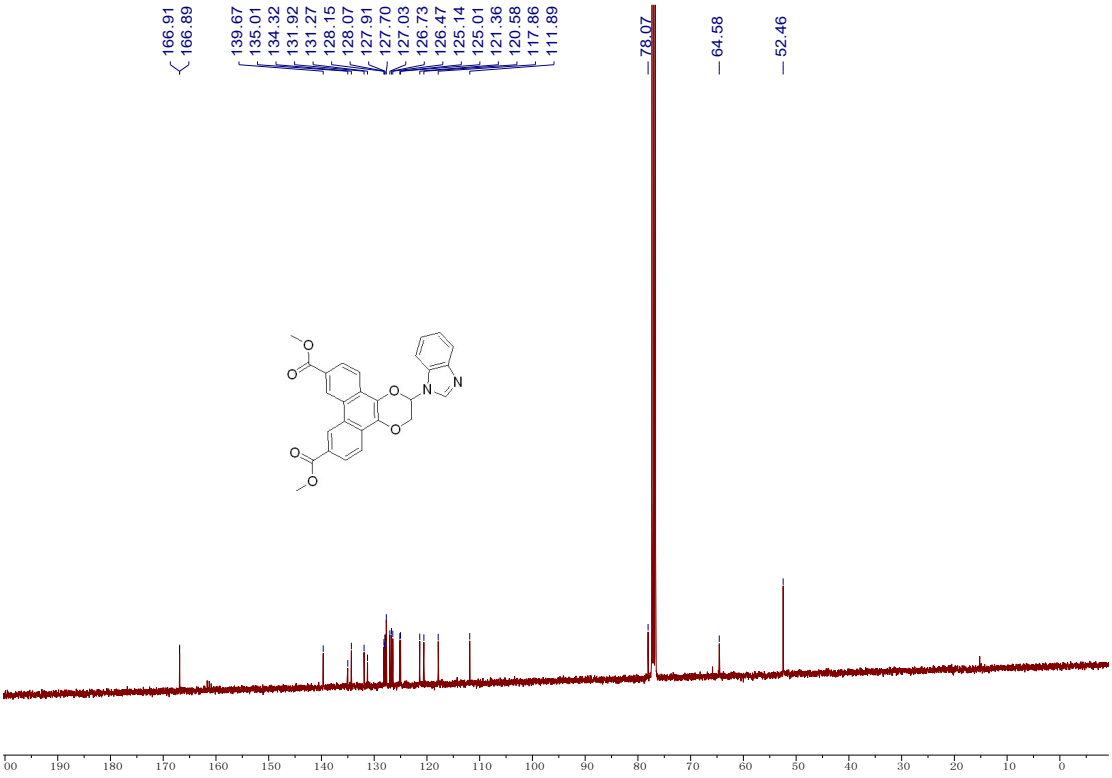
^{12}C NMR of PQ2-N4



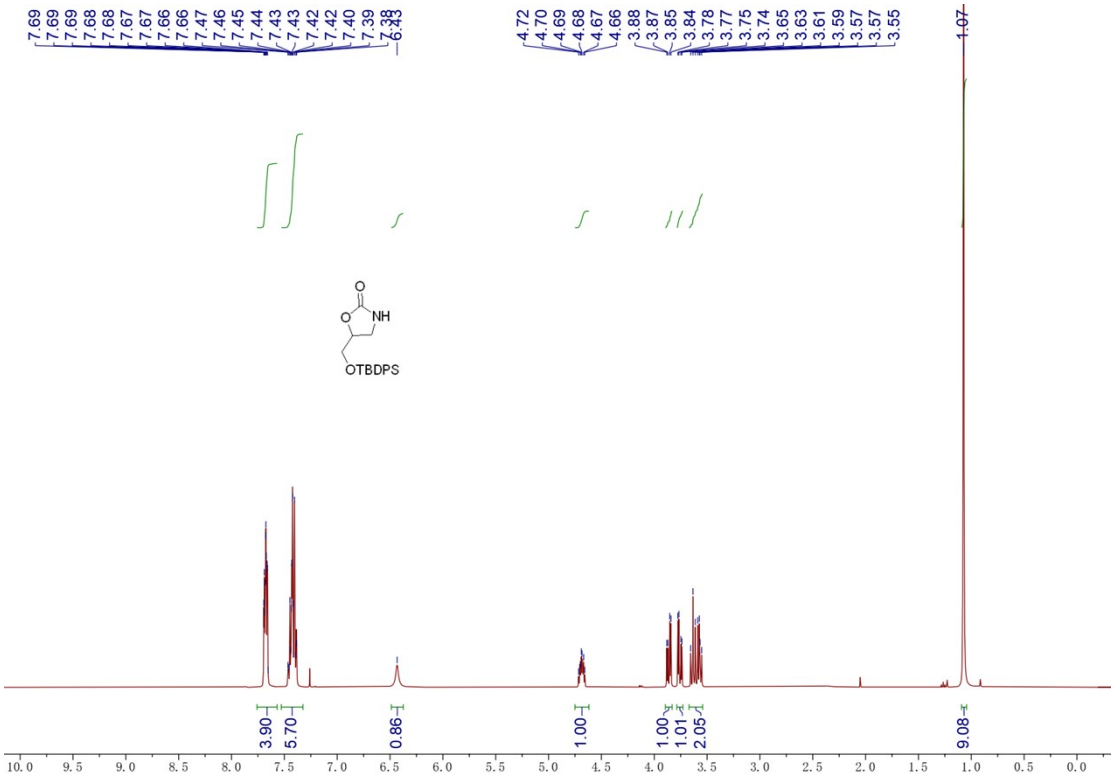
^{1}H NMR of PQ2-N6



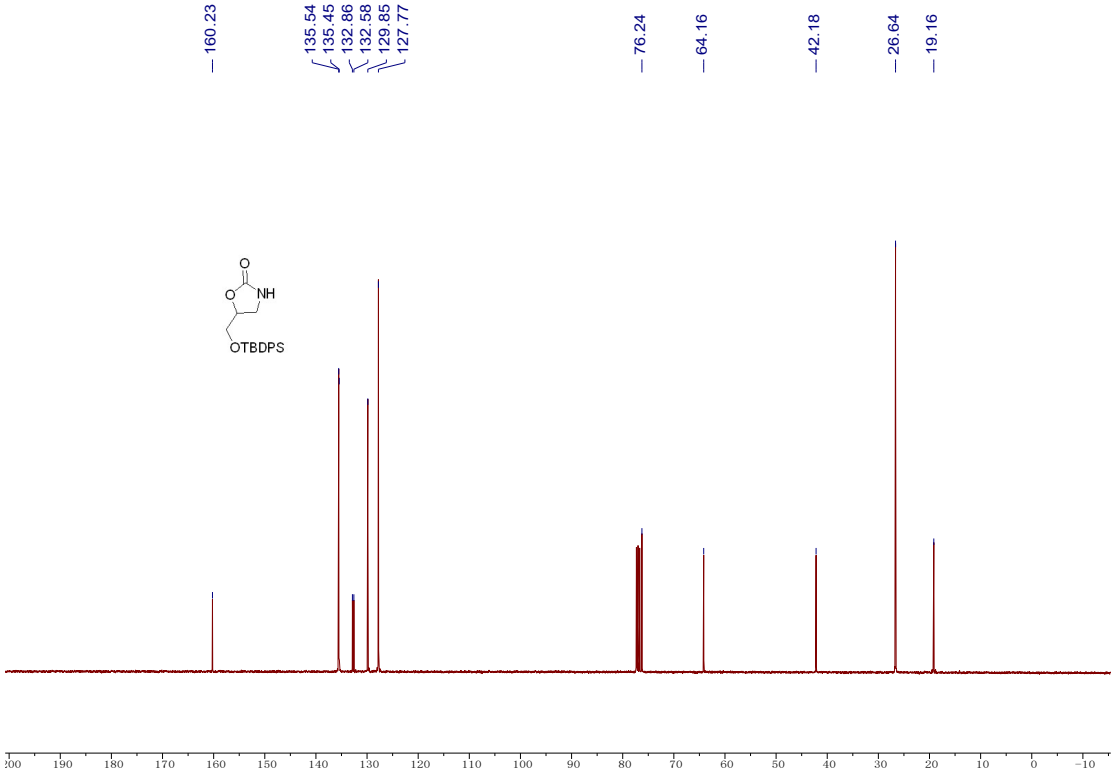
^{12}C NMR of PQ2-N6



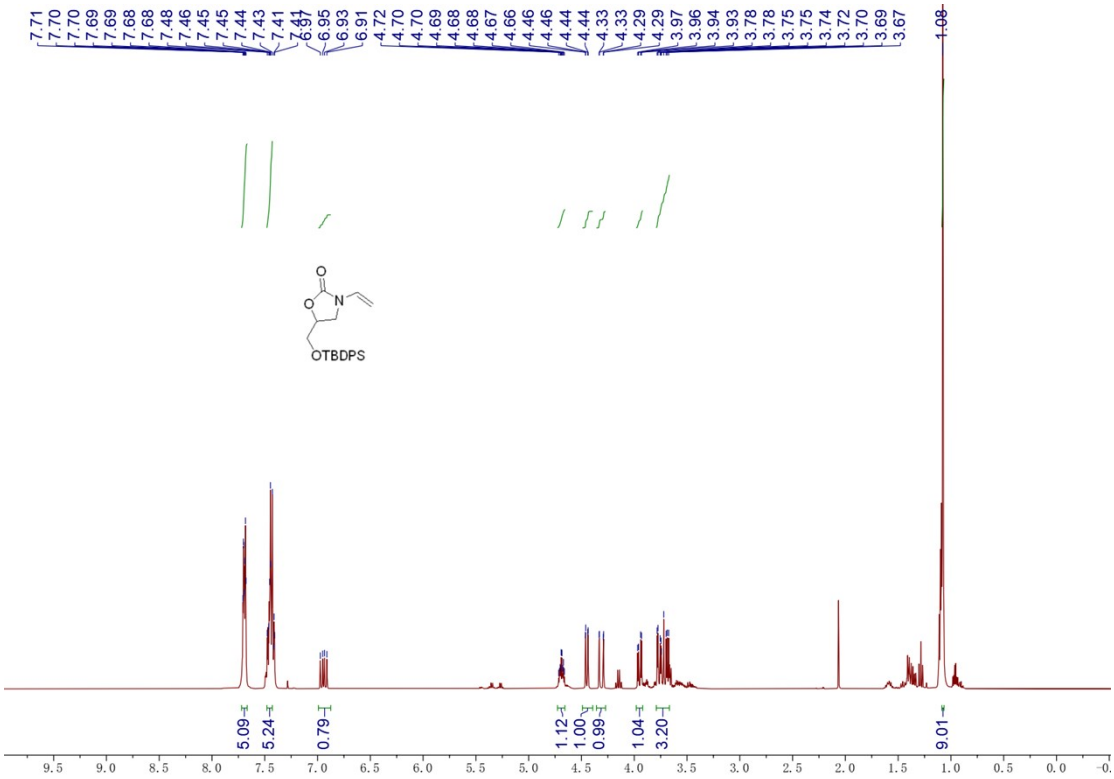
^{1}H NMR of 4a



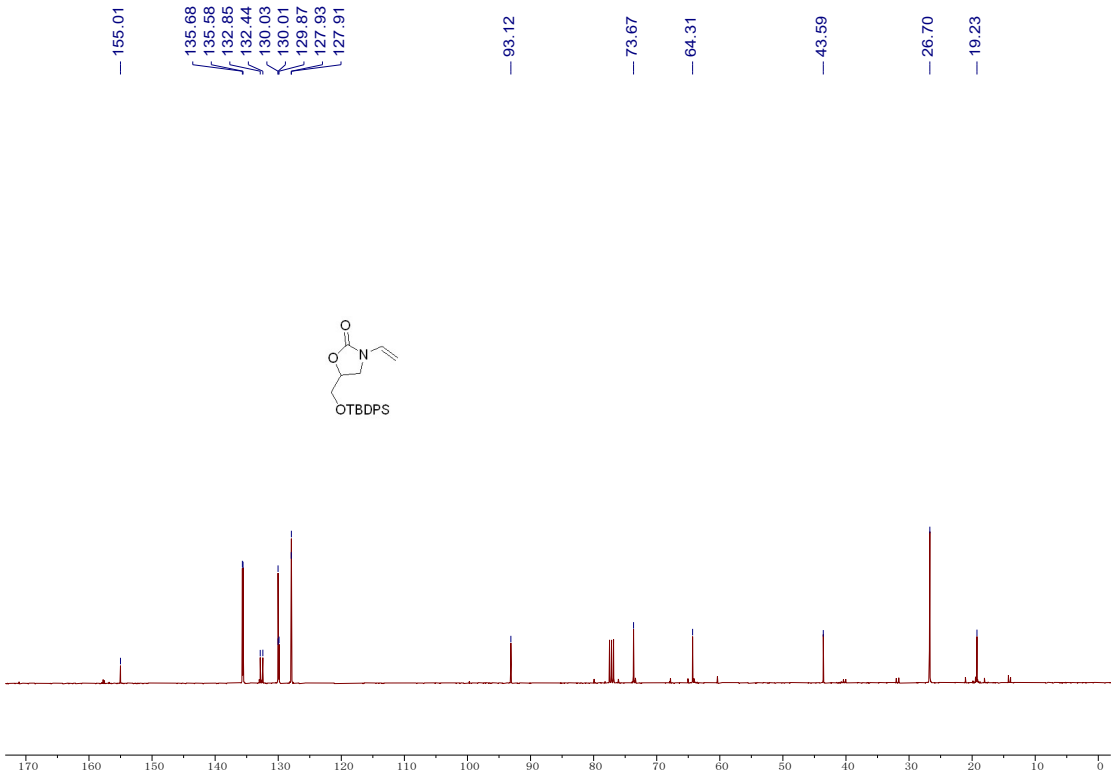
^{12}C NMR of 4a



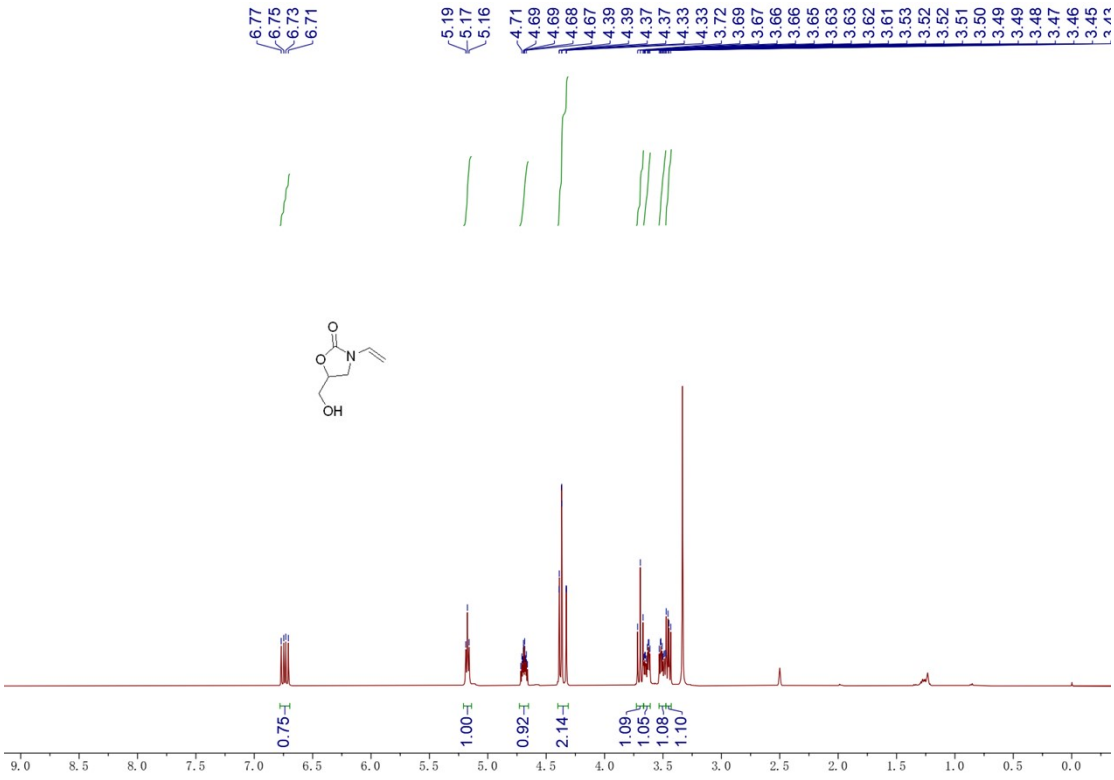
^{1}H NMR of 4b



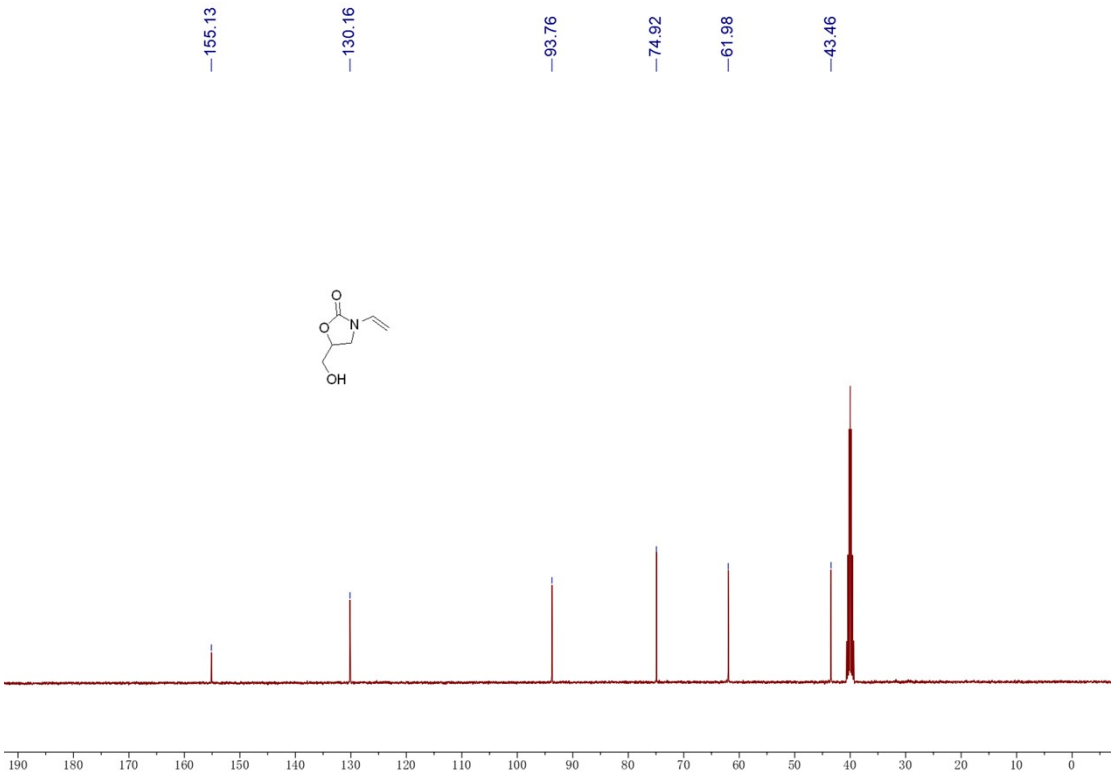
^{12}C NMR of 4b



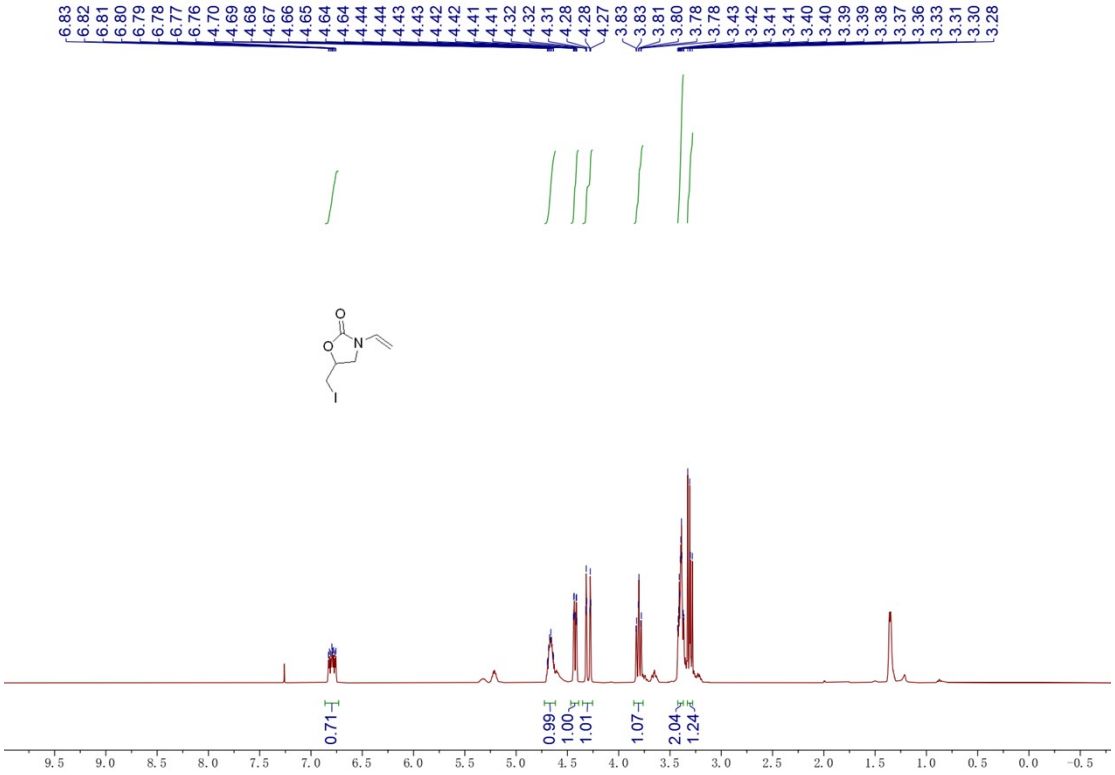
^{1}H NMR of 4c



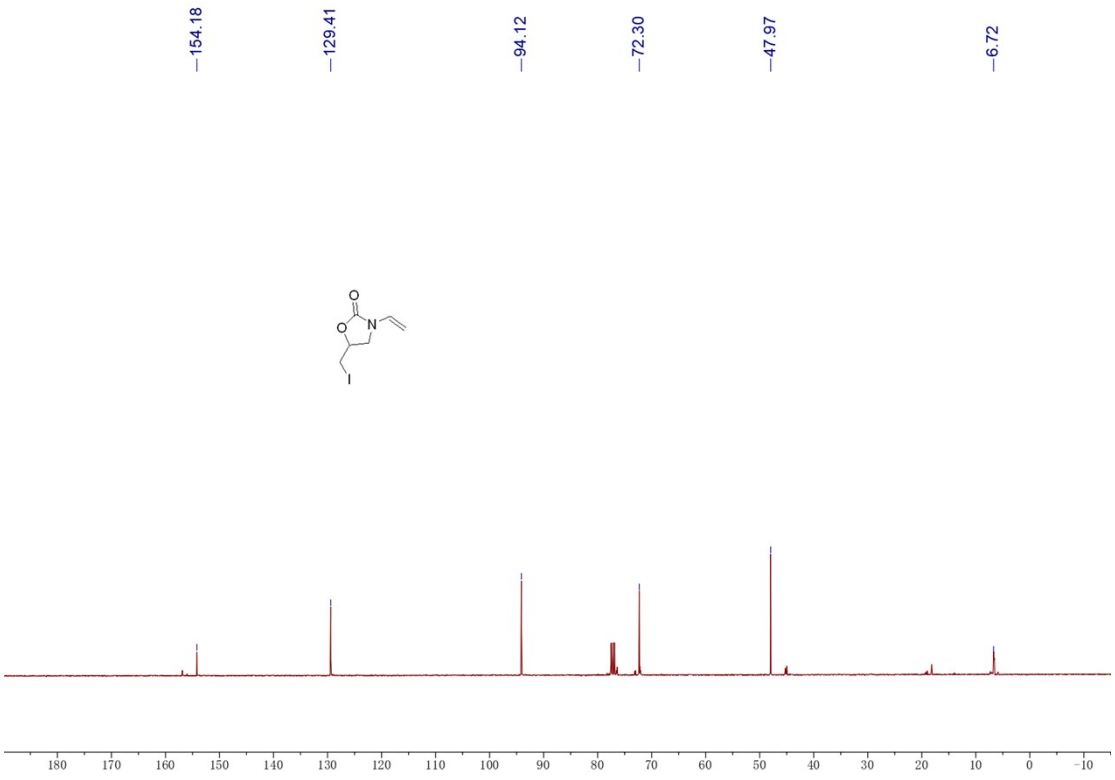
^{12}C NMR of 4c



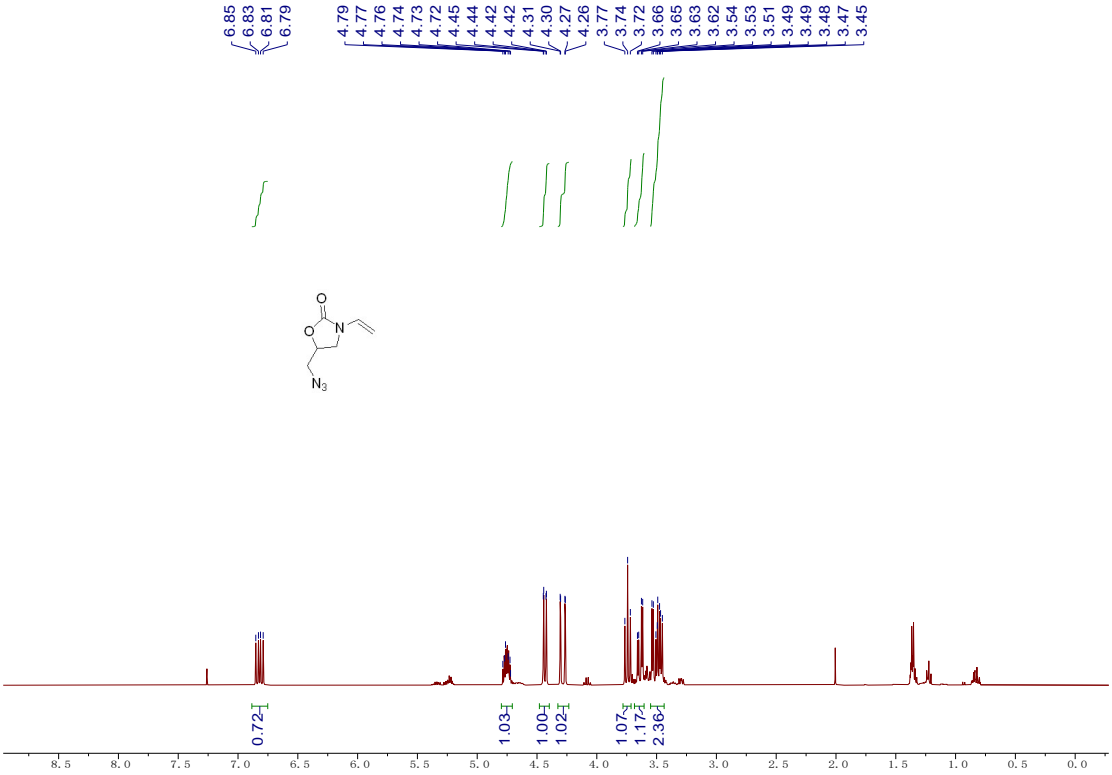
^{1}H NMR of 4d



^{12}C NMR of 4d



^{1}H NMR of Az-N4



^{12}C NMR of Az-N4